

Review Article

Perovskite Thin Film Solar Cells Based on Inorganic Hole Conducting Materials

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Organic-inorganic metal halide perovskites have recently shown great potential for application, due to their advantages of low-cost, excellent photoelectric properties and high power conversion efficiency. Perovskite-based thin film solar cells have achieved a power conversion efficiency (PCE) of up to 20%. Hole transport materials (HTMs) are one of the most important components of perovskite solar cells (PSCs), having functions of optimizing interface, adjusting the energy match, and helping to obtain higher PCE. Inorganic p-type semiconductors are alternative HTMs due to their chemical stability, higher mobility, high transparency in the visible region, and applicable valence band (VB) energy level. This review analyzed the advantages, disadvantages, and development prospects of several popular inorganic HTMs in PSCs.

1. Introduction

Perovskite solar cells (PSCs) based on organic-inorganic metal halide perovskites have recently attracted considerable attention as the power conversion efficiency (PCE) has increased dramatically from the initial 3.9% in 2009 to current 22.1% in a short span of several years [1–8]. Previous results demonstrated that PSCs may be the first in the history of photovoltaics (PV) combining high efficiency with low cost. The configurations of PSCs were evolved from dye-sensitized solar cells (DSSCs), and the key materials for the perovskite are compounds with the chemical formula ABX_3 ($A = CH_3NH_3$, $B = Pb$ or Sn , and $X = Cl$, Br , or I), which have received extensive attention due to their favorable photovoltaic properties [9, 10]. Generally, the device structure of PSCs can be categorized into mesoporous structure (Figure 1(a)) and planar junction structure (Figure 1(b)) [11]. The main function of perovskite is absorbing light to generate and transmit electron-hole pairs under continuous illumination. Then, the electrons and holes pass through the perovskite and shift to electron-transporting layer (ETL) and

hole transport layer (HTL), respectively, to generate current, as schematic presented in Figure 1(c).

While although a mass of efforts such as solvent additives, molecular dipoles, or interface modification has been devoted to optimize device efficiency, none of the present PSCs provides high PCE with long-term stability. Undoubtedly, a lack of confirmed stability may become the biggest barrier on the path of PSCs towards commercialization. HTL is one of the most important components of PSCs, having functions of optimizing interface, adjusting the energy-match, and helping obtain higher PCE, which has a great effect on device performance and stability [12–14]. Poly(3,4-ethylenedioxythiophene)-polystyrenesulfonate (PEDOT:PSS) and 2,2',7,7'-tetrakis(N,N-di-p-methoxyphenylamine)-9,9-spirobifluorene (spiro-OMeTAD) have been widely employed as HTL in the field of PSCs. Although PSCs that applied PEDOT:PSS and spiro-OMeTAD as HTL have obtained high PCE, none of them can provide with long-term stability partly because of the problematic acidic and hygroscopic characteristics of the organic HTMs applied in PSCs [15, 16].

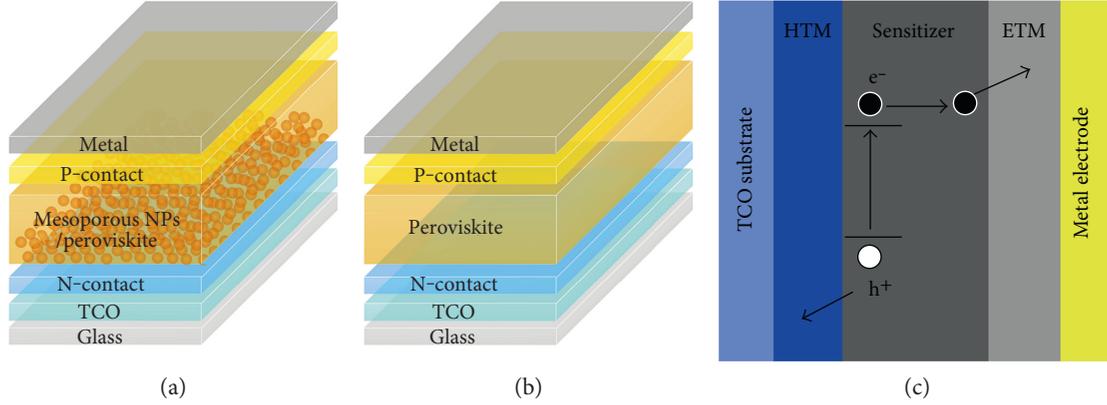


FIGURE 1: Device structures of (a) mesoporous structure, (b) n-i-p planar, planar junction structure, and (c) the scheme of carrier transport in PSCs.

TABLE 1: Device parameters for high-performance organometallic lead halide perovskite solar cells (PSCs) based on different inorganic hole transport materials (HTMs), the band gap, and deposition method of these HTMs.

HTM	Band gap (eV)	Deposition method	V_{oc} (V)	J_{sc} (mA/cm ²)	FF (%)	PCE (%)	Reference
NiO	3.5	ALD	1.04	21.87	72	16.40	[37]
Cu:NiO	$x > 3.5$	Solution-processed	1.12	19.17	73	15.40	[24]
Mg:Li:NiO	$x > 3.5$	Solution-processed	1.07	20.62	75	18.40	[36]
CuI	3.1	Solution-processed	1.04	21.06	62	13.58	[40]
CuSCN	3.8	Electrodeposition	1.00	21.90	76	16.60	[46]
CuO	1.3	Solution-processed	1.06	15.82	72	12.16	[52]
Cu ₂ O	2.1	Solution-processed	1.07	16.52	75	13.35	[52]
MoO ₃	3.4	Thermal decomposition	1.00	21.49	69	14.87	[53]
VO _x	2.42	Solution-processed	0.90	22.29	71	14.23	[55]

Recently, to improve the stability and reduce the cost of PSCs, various inorganic hole transport materials have been discovered and applied. In this review, PSCs employing different inorganic HTMs as hole transport layer (HTL) have been discussed and summarized. To date, a series of p-type inorganic metal compounds have been employed in PSCs, such as CuI [17], CuSCN [18–20], NiO [21–26], CuO [27], Cu₂O [27, 28], MoO₃ [29–31], and VO_x [32]. Compared to organic HTMs, inorganic p-type semiconductor materials have the advantages of high hole mobility, wide band gap, low cost, and solution-processed availability, which show promising prospects as hole-selective contacts in perovskite solar cells.

2. Inorganic HTMs for PSCs

There are some general requirements for inorganic HTMs used in PSCs, such as high transparency in the visible region, well chemical stability, higher mobility, and applicable valence band (VB) energy level. At present, inorganic HTMs such as CuI, CuSCN, NiO, CuO, Cu₂O, MoO₃, and VO_x have already been used in PSCs and the solar cells employing inorganic p-type semiconductors as HTLs exhibited improvement in device performance and stability.

Table 1 presents the band gap and deposition method of various HTMs reported in the literatures, as well as their photovoltaic parameters of top-performing PSCs based on these HTMs. In the following, we will analyze and discuss these frequently used inorganic HTMs, respectively.

2.1. NiO. NiO is a well-known p-type semiconductor widely used as a p-sensitization electrode for DSSCs and a hole-selective contact for organic bulk heterojunction solar cells [33, 34].

Initially, NiO was widely applied in DSSCs. In recent years, nickel oxide (NiO) as a promising HTM has been studied by several groups. In 2014, the first announced PCE of PSCs using nickel oxide as HTL was up to 7.8% [35]. Then, NiO nanocrystals (NCs) were obtained by a simple sol-gel process adopted as the hole transport layer in an inverted PSC, which observed a high PCE of 9.11% [25]. In 2015, copper- (Cu-) doped NiO (Cu:NiO) as HTL of planar heterojunction PSCs achieved a PCE of 15.4% [24]. At present, the highest recorded PCE of PSCs using Li, Mg-codoped NiO (Li_{0.05}Mg_{0.15}Ni_{0.8}O) as HTL was 18.4% [36]. This study developed heavily p-doped (p⁺) Ni_xMg_{1-x}O to extract photogenerated hole from perovskite layer, and large size (>1 cm²) PSCs with an efficiency of up to 16.2% were

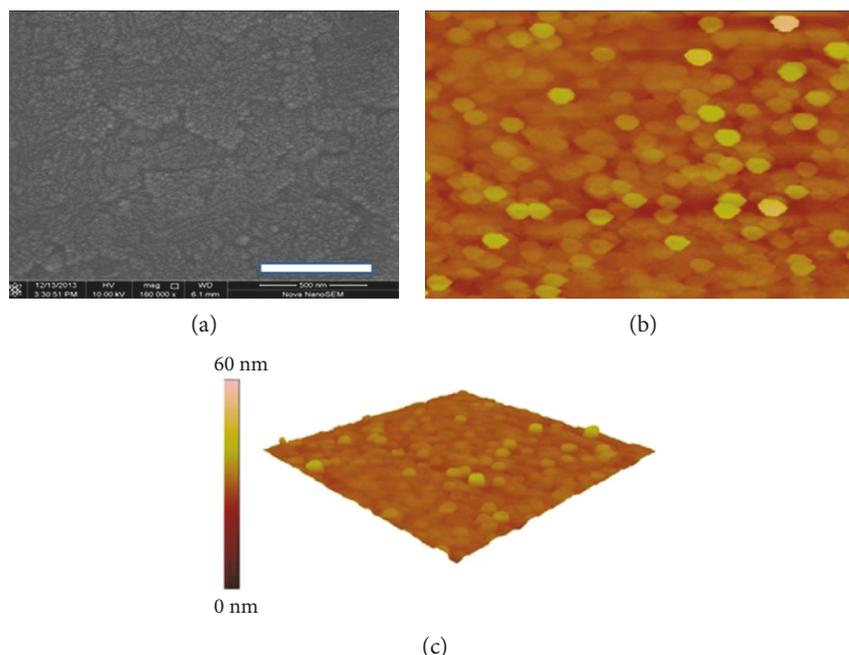


FIGURE 2: (a) SEM NiO film prepared by spin coating, (b) and (c) AFM of NiO film prepared by spin coating. Reprinted with permission from [21].

successfully fabricated. The latest reported PCE of PSCs employing pure NiO as HTL is up to 16.4%, and the NiO film was gotten by the atomic layer deposition (ALD) method [37].

NiO become a potential candidate for HTL, as its p-type characteristics of high optical transmittance, wide band gap ($E_g > 3.50$ eV), chemical stability, and an applicable valence band match with common light photoactive layers [33, 38]. The synthetic methods of NiO can be categorized into solution-processed and sol-gel, and NiO films can be prepared by various methods, such as pulsed laser deposition, electrodeposition, spray pyrolysis, spin coating, sputtering, and ALD method [37]. A frequently used method for preparing NiO is solution-processed technique by adding monoethanolamine and nickel acetate tetrahydrate in methoxyethanol then stirring for 10 hours to form NiO precursor solutions and via spin coating to achieve NiO film. The NiO film obtained by this way was composed of NiO nanoparticles (NCs), and the whole film was crack-free and smooth, as schematic presented in SEM and AFM (Figures 2(a), 2(b), and 2(c)). The photoluminescence (PL) quenching of perovskite based on NiO showed favorable charge transfer compatibility, presented in Figure 3. Perovskite excitation is at around 760 nm. Finally, PSC with NiO prepared by the above method as HTL obtained a 7.6% device performance [21].

Another common approach to achieve NiO is a simple sol-gel process. NiO film was fabricated by spin coating the sol-gel solution. This kind of NiO nanocrystal film with a flat and smooth surface guarantees the formation of a continuous and close-knit HTLs of PSCs as schematic presented in Figures 4(a) and 4(b). Hole extraction and transport properties of this film interfaced with the perovskite film were

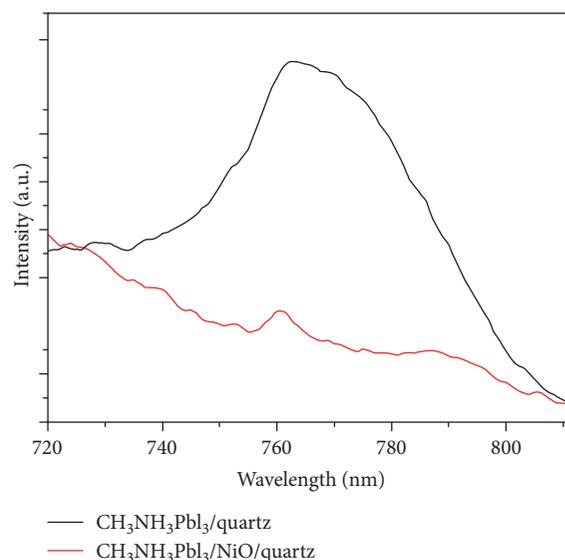


FIGURE 3: Photoluminescence spectra (excited by 600 nm laser) of $\text{CH}_3\text{NH}_3\text{PbI}_3$ film deposited on top of NiO film or quartz substrate. Reprinted with permission from [21].

higher than those of organic HTLs, such as PEDOT:PSS, and perovskite deposited on NiO NC films is with homogeneous phase. The PSCs with HTL of NiO NC film at a thickness of around 35 nm exhibited the best PCE of 9.11%, as showed in Figure 4(c) [25].

Recently, ALD method has been used to fabricate ultrathin pure un-doped NiO films. And PSCs employing this kind of NiO film as HTL achieved a high PCE of 16.4%. We can fabricate highly sequential and dense ultrathin films at nanometer size following the ALD method.

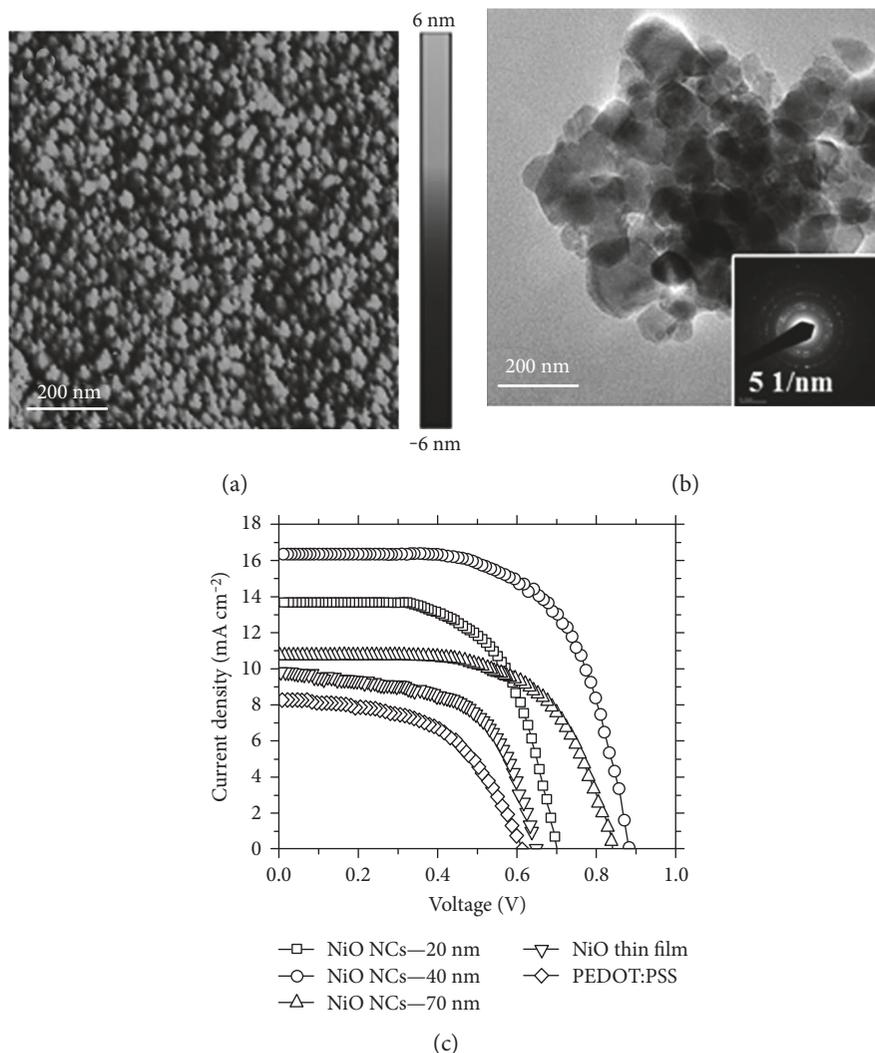


FIGURE 4: (a) AFM roughness image of a NiO nanocrystal film on FTO. (b) Bright-field TEM image of a sample of NiO NCs with the corresponding diffraction pattern (inset). (c) Typical J-V curves of the perovskite solar cells with different NiO hole transport layers and PEDOT:PSS. Reprinted with permission from [25].

The effective work function (WF) of ultrathin NiO apparently increased, which enormously promoted the hole extraction performance. In addition, ultrathin NiO films have a higher transparency which highly contribute to the photovoltaic devices. The freshly ultrathin pure undoped NiO films deposited as HTL of PSCs exhibited a high PCE of 16.4% with $J_{sc} = 21.9 \text{ mA cm}^{-2}$, $V_{oc} = 1.04 \text{ V}$, and $FF = 0.72$ [37].

A salient weakness with PSCs' use of NiO as HTL is that it is hard for NiO to support an ultrathin perovskite film (<60 nm) [22, 23], which has still limited the development of PCE of PSCs using NiO as HTLs. Another shortage with PSCs employing NiO as HTL is that FF and V_{oc} are lower than the common organic HTMs, in particular when the NiO was achieved by the solution-processed method. These parameters greatly affect the device performance [37].

Briefly speaking, an ideal p-NiO film for high PV performance should (1) have high transparency, (2) have favorable hole extraction and transport performance properties,

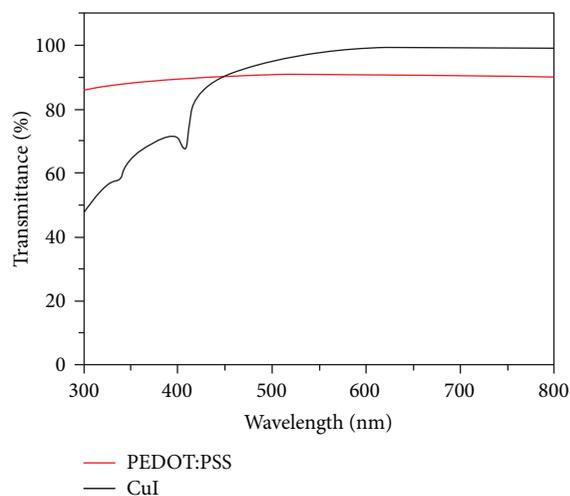


FIGURE 5: Optical transmission spectra of the PEDOT:PSS film and CuI film. Reprinted with permission from [40].

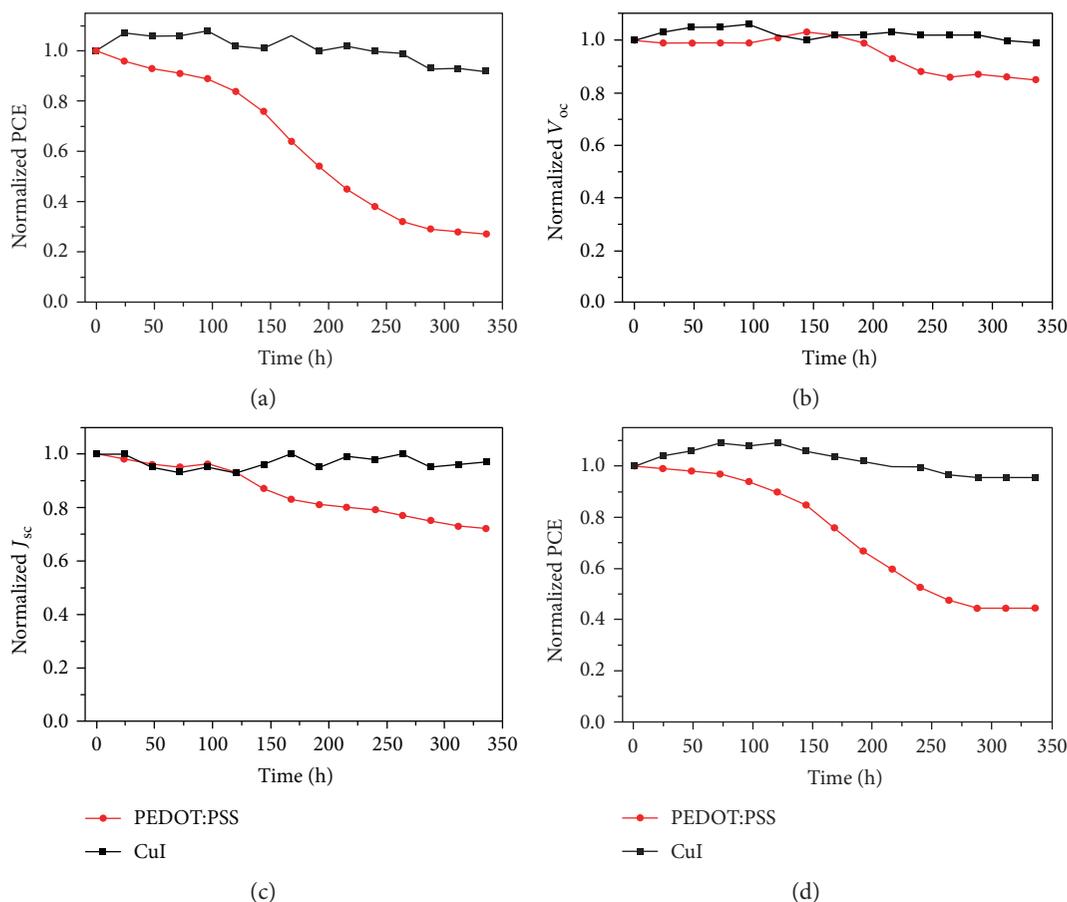


FIGURE 6: Normalized PCE (a), V_{oc} (b), J_{sc} (c), and FF (d) of perovskite solar cells employing CuI and PEDOT:PSS HTLs as a function of storage time in air. Reprinted with permission from [40].

(3) have applicable energy levels, and (4) have low cost and easy access [33].

2.2. CuI. Inorganic p-type semiconductor copper iodide (CuI) becomes one of the promising HTLs for PSCs, due to its admirable properties such as wide band gap, high conductivity, low cost, and solution processable. At the beginning, CuI as hole conductors was employed in DSSCs and quantum dot-sensitized solar cells. In recent years, several groups have used CuI as HTLs for PSCs, and the first application of CuI for PSCs has successfully achieved a potential PCE of 6.0% [17]. Then, the PCE of PSCs using CuI as HTL increased to 7.5% [39]. In 2015, the PCE of PSCs applying CuI as HTL in inverted planar heterojunction perovskite solar cells reach up to 13.8% [40]. At present, the highest announced PCE of PSCs using CuI as HTL is 16.8% [41].

Solution-processed method is the frequently used approach to acquire CuI. The CuI films were prepared by spin coating CuI precursor solution in inert gas. Compared to PEDOT:PSS, CuI films exhibit higher transmittance in visible light from 450 to 800 nm (Figure 5), which make it potential to be used as a HTL. In addition, high transparency can allow more photo flux reach perovskite active layer to generate intense photocurrent. However, the surface morphology of CuI films is rough when compared to PEDOT:PSS

films, which may be because of the existence of large CuI grains [40].

At present, PSCs employing CuI as HTLs have achieved a relatively high PCE of 13.58% [40]. Above all, PSCs using CuI as the HTL exhibited improved air stability when compared to PSCs employing PEDOT:PSS as the HTL (Figure 6). In this respect, CuI is an excellent choice, because long-term stability of PSCs is of vital significance for practical applications [40].

Although PSCs using CuI as HTLs can replace conventional organic HTMs, the device open-circuit voltage (V_{oc}) is relatively low mainly because of a high recombination rate as determined by impedance spectroscopy. There are still numerous challenges in the optimization of PSC-employed CuI as HTLs. The primary problems include (1) how to control the surface morphology of CuI, (2) how to achieve favorable contacts between CuI layer and perovskite layer, and (3) how to dissolve CuI and eliminate large CuI grains.

2.3. CuSCN. As mentioned above, copper thiocyanate (CuSCN) appears to be a good candidate of inorganic HTLs for its internal p-type characteristics of a wide band gap and high optical transparency [42–44].

CuSCN was first applied in mesoporous PSCs by Ito et al. with a device structure of FTO/TiO₂/TiO₂/CH₃NH₃PbI₃/

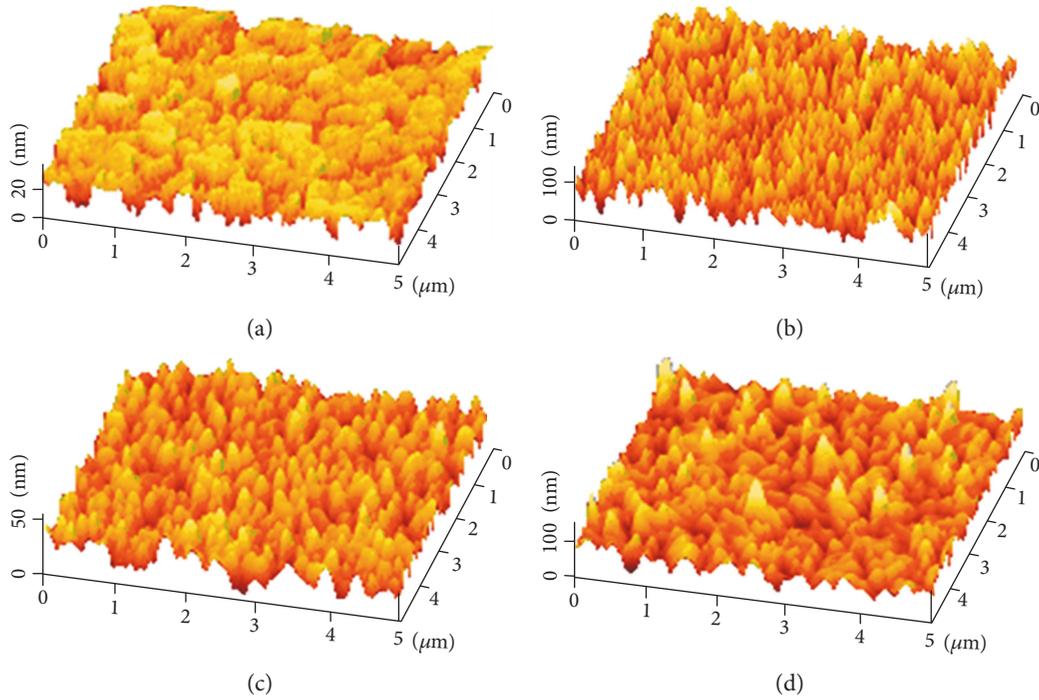


FIGURE 7: AFM images of ITO/glass (a), CuSCN/ITO/glass (b), $\text{CH}_3\text{NH}_3\text{PbI}_3$ (one-step)/CuSCN/ITO/glass (c), and $\text{CH}_3\text{NH}_3\text{PbI}_3$ (two-step)/CuSCN/ITO/glass (d). The RMS roughness values are 4.6, 19.3, 7.6, and 17.0 nm, respectively. Reprinted with permission from [46].

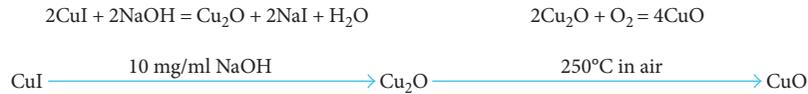


FIGURE 8: Preparation process for Cu_2O and CuO films.

CuSCN/Au and achieved a PCE of 4.85% in 2013 [18]. Soon after, planar PSCs using CuSCN as a HTL received a PCE of 6.4%. There were reported low PCEs of PSCs based on CuSCN mainly because of the poor quality of $\text{CH}_3\text{NH}_3\text{PbI}_3$ active layer films on top of the CuSCN layers. Grätzel et al. enhanced the device PCE to 12.4% [45], via optimizing perovskite surface morphology by two times of iodide deposition. Then, the PCE of the CuSCN-based PSCs has already been improved to 16.6% [46, 47]. The latest announced PCE of PSCs using CuI as HTL has reached up to 18% [48]. In spite of the relatively low PCE compared to efficiency of PSCs based on organic HTMs, the low cost and air stability of CuSCN make it become a promising inorganic HTM.

The high PCE (16.6%) photovoltaic device used a one-step fast deposition method to fabricate high-quality perovskite films based on a rough CuSCN. $\text{CH}_3\text{NH}_3\text{PbI}_3$ prepared by a one-step faster deposition method with lower surface roughness and smaller interface contact resistance was compared to the perovskite films prepared by a conventional two-step deposition process, as showed in Figure 7 [46, 49].

Although cells using CuSCN as HTL have achieved considerable device efficiency, the CuSCN layer was fabricated via electrodeposition, which needs to be carefully

compounded from a precursor solution containing potassium thiocyanate (KSCN), copper sulfate (CuSO_4), and ethylenediaminetetraacetic acid (EDTA). And the CuSCN films achieved by the above method are relatively rough and unshaped, which affect further improvements of PSCs [46].

2.4. Cu_2O and CuO. CuO and Cu_2O are well-known p-type semiconductors [27, 28, 50]. There is a simple low-temperature method to synthesize Cu_2O and CuO films and employ them as HTL for PSCs. Traditional methods for preparing Cu_2O film are thermal oxidation, sputtering, electrodeposition, and metal-organic chemical vapor deposition [51]. Cu_2O film can be obtained via in situ conversion of CuI film in aqueous NaOH solution, and CuO film is fabricated by heating Cu_2O film in the air, as showed in Figure 8 [52].

PSCs using Cu_2O and CuO as HTMs show observably increased V_{oc} , J_{sc} , and PCE. Recently, PSCs using Cu_2O and CuO as HTLs exhibited PCE of 13.35% and 12.16%, respectively [52]. Additionally, NH_4Cl was added into $\text{CH}_3\text{NH}_3\text{PbI}_3$ precursor to improve crystallinity of perovskite in Li et al. study. The increased V_{oc} mainly owns the VB of Cu_2O and CuO well matching with VB of the

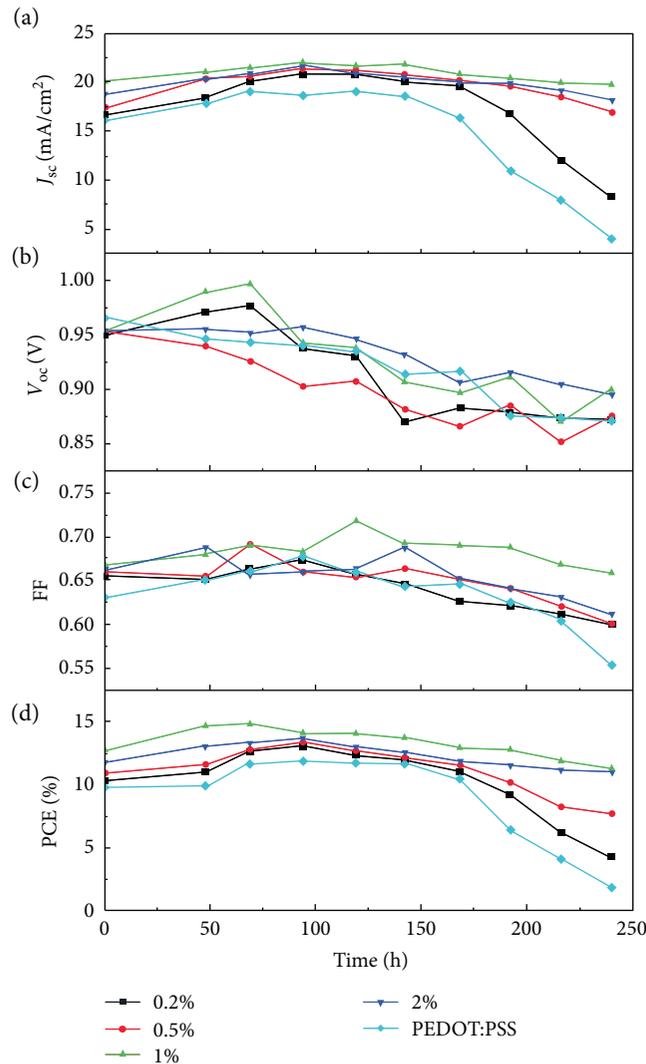


FIGURE 9: (a) J_{sc} , (b) V_{oc} , (c) FF, and (d) PCE values as a function of aging time of the devices with different MoO₃/PEDOT:PSS and pristine PEDOT:PSS HTLs. Reprinted with permission from [53].

perovskite and favorable crystallinity of perovskite on Cu₂O and CuO. What is more, well crystallinity enhanced the charge carrier transport and increased J_{sc} .

Compared to the PSCs employing NiO or Cu:NiO as HTLs, Cu₂O-based cells showed a superior property due to the higher mobility of Cu₂O, less energy loss, and favorable perovskite surface morphology on Cu₂O film [21].

2.5. MoO₃. MoO₃ is another potential HTM owing to the advantage of nontoxicity and air stability. However, PSCs with MoO₃ as HTL exhibit a low PCE mainly because of the poor quality of perovskite films deposited on MoO₃ [29, 31].

MoO₃ is a good HTM, but the poor perovskite films deposited on top of it limit further improvement. In order to solve the difficult problem, one simple solution would be to use an MoO₃/PEDOT:PSS composite film as the HTL in PSCs to take advantage of the ambient condition stability and favorable photovoltaic properties of MoO₃ and at the same time guarantee the admirable surface morphology of perovskite film [53].

Li et al. used a MoO₃/PEDOT:PSS bilayer structure as the HTL for PSCs. MoO₃ was prepared by a thermal decomposition of ammonium heptamolybdate ((NH₄)₆Mo₇O₂₄·4H₂O) solution at 80°C. The PSCs have a structure of ITO/MoO₃/PEDOT:PSS/CH₃NH₃PbI₃/C60/Bphen/Ag. The application of an MoO₃ layer between ITO and PEDOT:PSS not only enhanced the hole extraction efficiency from perovskite to the ITO electrode but also avoided direct contact between rough MoO₃ and CH₃NH₃PbI₃. By this way, we can obtain a high-quality perovskite films deposited on top of PEDOT:PSS. These improvements contribute to the increase of stability and PCE of PSCs compared to the cells employing only PEDOT:PSS. Finally, the optimized PSCs exhibit a PCE of 14.87% [53]. What is more, the device stability increases when a MoO₃ layer is inserted between ITO and PEDOT:PSS as showed in Figure 9 [53].

2.6. VO_x. VO_x has become a favorable p-type semiconductor material primarily due to its higher work function (WF) and stability, and it can be prepared by low-temperature

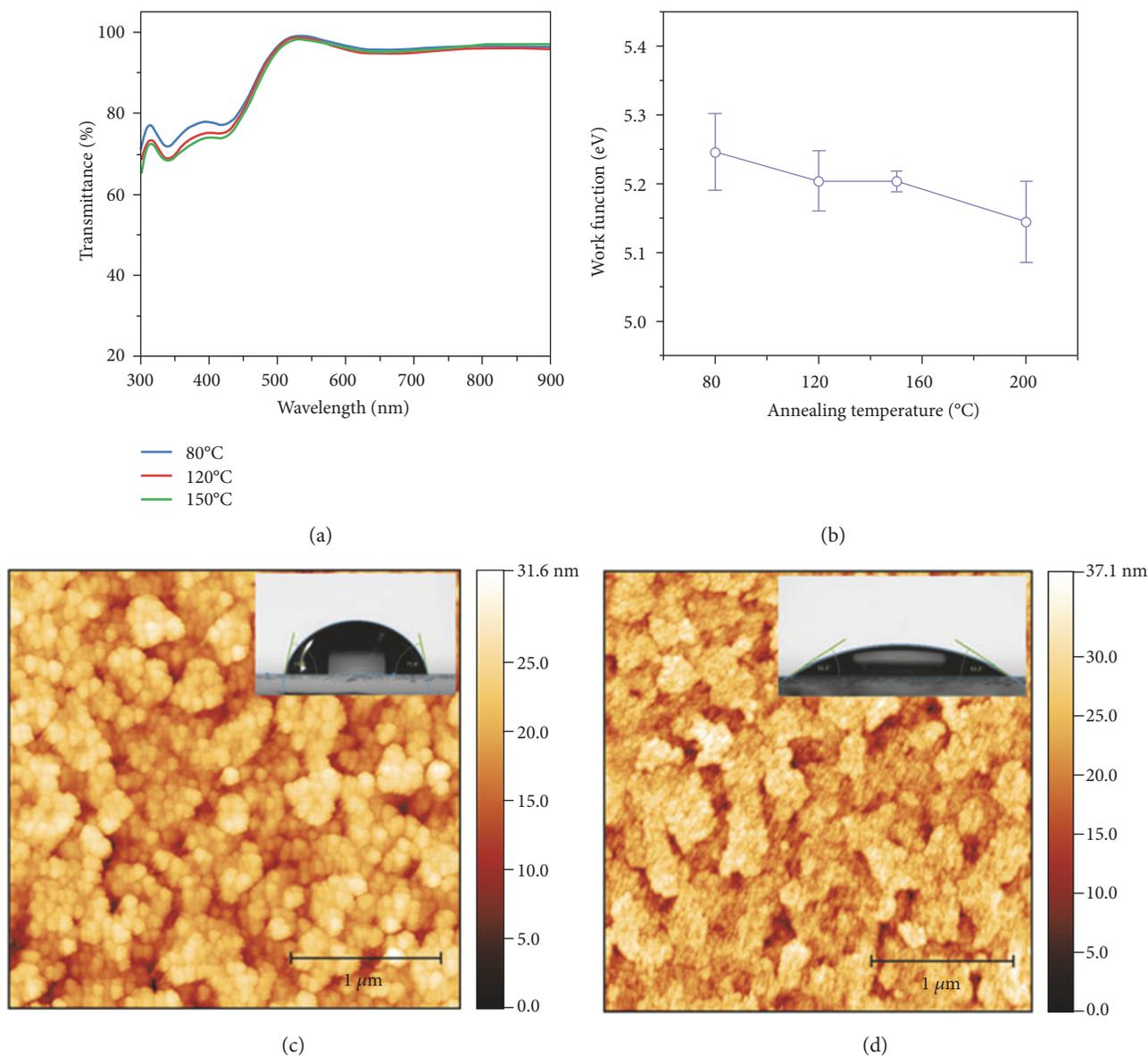


FIGURE 10: (a) Transmittance spectra of VO_x layers annealed at different temperatures. (b) Work function of VO_x layers annealed at different temperatures on ITO substrates. (c) AFM images of a bare ITO substrate. (d) AFM images of a VO_x -coated ITO substrate. Reprinted with permission from [55].

solution-processed method [32, 54]. At the beginning, VO_x was used as HTL in organic solar cells (OSCs). Recently, VO_x occurred as HTL for PSCs and achieved a relatively high PCE of 14.23% [55].

In general, VO_x films are fabricated by spin coating and annealed sol-gel precursor solution of VO_x . And the measurements of the VO_x layer exhibit high transmittance and well-quenching efficiency (Figure 10(a)). The value of x in VO_x was calculated at about 2.428 via X-ray photoelectron spectroscopy (XPS). High WF (Figure 10(b)) of VO_x not only extremely benefits cells containing high ionization potential donor materials but also reduces losses in V_{oc} and series resistance (R_s) [55]. However, VO_x is still faulty for its poor surface morphology result in harsh

deposition of perovskite films, as shown in Figures 10(c) and 10(d) [24, 45].

3. Conclusion

Inorganic semiconductor materials can be employed as hole-selective materials for PSCs due to their advantages of high hole mobility, wide band gap, and low cost, and they could be obtained by solution-processed method, showing promising respect of inorganic HTMs. What is more, the application of inorganic HTMs can enormously increase the stability and reduce cost of cells, which is very significant for PSCs. However, the reported device performance of most of the inorganic hole conductor-based PSCs

is still much lower than that of cells with organic HTMs, which may result in the poor quality of perovskite films on top of the inorganic HTL.

Conflicts of Interest

The authors declare that there is no conflict of interest regarding the publication of this paper.

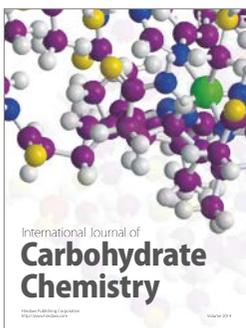
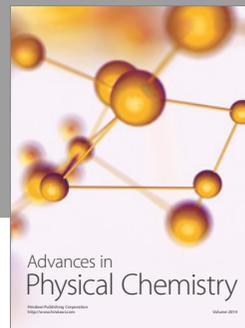
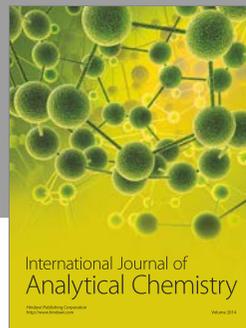
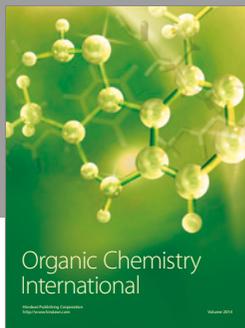
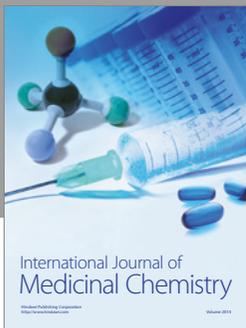
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References

- [1] A. Kojima, K. Teshima, Y. Shirai, and T. Miyasaka, "Organometal halide perovskites as visible-light sensitizers for photovoltaic cells," *Journal of the American Chemical Society*, vol. 131, no. 17, pp. 6050–6051, 2009.
- [2] H. Zhou, Q. Chen, G. Li et al., "Interface engineering of highly efficient perovskite solar cells," *Science*, vol. 345, no. 6196, pp. 542–546, 2014.
- [3] W. S. Yang, J. H. Noh, N. J. Jeon et al., "High-performance photovoltaic perovskite layers fabricated through intramolecular exchange," *Science*, vol. 348, no. 6240, pp. 1234–1237, 2015.
- [4] N. J. Jeon, J. H. Noh, W. S. Yang et al., "Compositional engineering of perovskite materials for high-performance solar cells," *Nature*, vol. 517, no. 7535, pp. 476–480, 2015.
- [5] Z. Yu and L. Sun, "Recent progress on hole-transporting materials for emerging organometal halide perovskite solar cells," *Advanced Energy Materials*, vol. 5, no. 12, 2015.
- [6] S. Albrecht, M. Saliba, J. P. Baena et al., "Monolithic perovskite/silicon-heterojunction tandem solar cells processed at low temperature," *Energy & Environmental Science*, vol. 9, no. 1, pp. 81–88, 2016.
- [7] H. S. Jung and N.-G. Park, "Perovskite solar cells: from materials to devices," *Small*, vol. 11, no. 1, pp. 10–25, 2015.
- [8] "NREL efficiency chart," June 2016, http://www.nrel.gov/ncpv/images/efficiency_chart.jpg.
- [9] G. Chen, J. Seo, C. Yang, and P. N. Prasad, "Nanochemistry and nanomaterials for photovoltaics," *Chemical Society Reviews*, vol. 42, no. 21, pp. 8304–8338, 2013.
- [10] M. A. Green, A. Ho-Baillie, and H. J. Snaith, "The emergence of perovskite solar cells," *Nature Photonics*, vol. 8, no. 7, pp. 560–514, 2014.
- [11] M.-H. Li, P.-S. Shen, K.-C. Wang, T. F. Guo, and P. Chen, "Inorganic p-type contact materials for perovskite-based solar cells," *Journal of Materials Chemistry A*, vol. 3, no. 17, pp. 9011–9019, 2015.
- [12] W. Yan, S. Ye, Y. Li et al., "Hole-transporting materials in inverted planar perovskite solar cells," *Advanced Energy Materials*, vol. 6, no. 17, 2016.
- [13] T. Leijtens, G. E. Eperon, N. K. Noel, S. N. Habisreutinger, A. Petrozza, and H. J. Snaith, "Stability of metal halide perovskite solar cells," *Advanced Energy Materials*, vol. 5, no. 20, article 1500963, 2015.
- [14] Y. Rong, L. Liu, A. Mei, X. Li, and H. Han, "Beyond efficiency: the challenge of stability in mesoscopic perovskite solar cells," *Advanced Energy Materials*, vol. 5, no. 20, article 1501066, 2015.
- [15] J. Liu, Y. Wu, C. Qin et al., "A dopant-free hole-transporting material for efficient and stable perovskite solar cells," *Energy & Environmental Science*, vol. 7, no. 9, pp. 2963–2967, 2014.
- [16] J. You, L. Meng, T.-B. Song et al., "Improved air stability of perovskite solar cells via solution-processed metal oxide transport layers," *Nature Nanotechnology*, vol. 11, no. 1, pp. 75–81, 2016.
- [17] J. A. Christians, R. C. M. Fung, and P. V. Kamat, "An inorganic hole conductor for organo-lead halide perovskite solar cells. Improved hole conductivity with copper iodide," *Journal of the American Chemical Society*, vol. 136, no. 2, pp. 758–764, 2014.
- [18] S. Ito, S. Tanaka, H. Vahlman, H. Nishino, K. Manabe, and P. Lund, "Carbon-double-bond-free printed solar cells from TiO₂/CH₃NH₃PbI₃/CuSCN/au: structural control and photoaging effects," *ChemPhysChem*, vol. 15, no. 6, pp. 1194–1200, 2014.
- [19] A. S. Subbiah, A. Halder, S. Ghosh, N. Mahuli, G. Hodes, and S. K. Sarkar, "Inorganic hole conducting layers for perovskite-based solar cells," *Journal of Physical Chemistry Letters*, vol. 5, no. 10, pp. 1748–1753, 2014.
- [20] S. Ito, S. Tanaka, K. Manabe, and H. Nishino, "Effects of surface blocking layer of Sb₂S₃ on nanocrystalline TiO₂ for CH₃NH₃PbI₃ perovskite solar cells," *The Journal of Physical Chemistry C*, vol. 118, no. 30, pp. 16995–17000, 2014.
- [21] L. Hu, J. Peng, W. Wang et al., "Sequential deposition of CH₃NH₃PbI₃ on planar NiO film for efficient planar perovskite solar cells," *ACS Photonics*, vol. 1, no. 7, pp. 547–553, 2014.
- [22] X. Yin, Z. Yao, Q. Luo et al., "High Efficiency Inverted Planar Perovskite Solar Cells with Solution-Processed NiOx Hole Contact," *ACS Applied Materials & Interfaces*, vol. 9, no. 3, pp. 2439–2448, 2017.
- [23] H. Tian, B. Xu, H. Chen, E. M. J. Johansson, and G. Boschloo, "Solid-state perovskite-sensitized p-type mesoporous nickel oxide solar cells," *ChemSusChem*, vol. 7, no. 8, pp. 2150–2153, 2014.
- [24] J. H. Kim, P.-W. Liang, S. T. Williams et al., "High-performance and environmentally stable planar heterojunction perovskite solar cells based on a solution-processed copper-doped nickel oxide hole-transporting layer," *Advanced Materials*, vol. 27, no. 4, pp. 695–701, 2015.
- [25] Z. Zhu, Y. Bai, T. Zhang et al., "High-performance hole-extraction layer of sol-gel-processed NiO nanocrystals for inverted planar perovskite solar cells," *Angewandte Chemie*, vol. 126, no. 46, pp. 12779–12783, 2014.
- [26] W. Chen, Y. Wu, J. Liu et al., "Hybrid interfacial layer leads to solid performance improvement of inverted perovskite solar cells," *Energy & Environmental Science*, vol. 8, no. 2, pp. 629–640, 2015.
- [27] L. C. Chen, C. C. Chen, K. C. Liang et al., "Nano-structured CuO-Cu₂O complex thin film for application in CH₃NH₃PbI₃ perovskite solar cells," *Nanoscale Research Letters*, vol. 11, no. 1, p. 402, 2016.
- [28] S. Chatterjee and A. J. Pal, "Introducing Cu₂O thin films as a hole-transport layer in efficient planar perovskite solar cell structures," *Journal of Physical Chemistry C*, vol. 120, no. 3, pp. 1428–1437, 2016.

- [29] Y. Zhao, A. M. Nardes, and K. Zhu, "Effective hole extraction using MoO_x -Al contact in perovskite $\text{CH}_3\text{NH}_3\text{PbI}_3$ solar cells," *Applied Physics Letters*, vol. 104, no. 21, p. 213906, 2014.
- [30] C. Liu, Z. Su, W. Li et al., "Improved performance of perovskite solar cells with a $\text{TiO}_2/\text{MoO}_3$ core/shell nanoparticles doped PEDOT:PSS hole-transporter," *Organic Electronics*, vol. 33, pp. 221–226, 2016.
- [31] Z.-L. Tseng, L.-C. Chen, C.-H. Chiang, S. H. Chang, C. C. Chen, and C. G. Wu, "Efficient inverted-type perovskite solar cells using UV-ozone treated MoO_x and WO_x as hole transporting layers," *Solar Energy*, vol. 139, pp. 484–488, 2016.
- [32] M. Xiao, M. Gao, F. Huang et al., "Efficient perovskite solar cells employing inorganic interlayers," *ChemNanoMat*, vol. 2, no. 3, pp. 182–188, 2016.
- [33] L. Alibabaei, H. Luo, R. L. House, P. G. Hoertz, R. Lopez, and T. J. Meyer, "Applications of metal oxide materials in dye sensitized photoelectrosynthesis cells for making solar fuels: let the molecules do the work," *Journal of Materials Chemistry a*, vol. 1, no. 13, pp. 4133–4145, 2013.
- [34] M. D. Irwin, B. Buchholz, A. W. Hains, R. P. H. Chang, and T. J. Marks, "*p*-type semiconducting nickel oxide as an efficiency-enhancing anode interfacial layer in polymer bulk-heterojunction solar cells," *Proceedings of the National Academy of Sciences of the United States of America*, vol. 105, no. 8, pp. 2783–2787, 2008.
- [35] J.-Y. Jeng, K.-C. Chen, T.-Y. Chiang et al., "Nickel oxide electrode interlayer in $\text{CH}_3\text{NH}_3\text{PbI}_3$ perovskite/PCBM planar-heterojunction hybrid solar cells," *Advanced Materials*, vol. 26, no. 24, pp. 4107–4133, 2014.
- [36] W. Chen, Y. Wu, Y. Yue et al., "Efficient and stable large-area perovskite solar cells with inorganic charge extraction layers," *Science*, vol. 350, no. 6263, pp. 944–948, 2015.
- [37] S. Seo, I. J. Park, M. Kim et al., "An ultra-thin, un-doped NiO hole transporting layer of highly efficient (16.4%) organic-inorganic hybrid perovskite solar cells," *Nanoscale*, vol. 8, no. 22, pp. 11403–11412, 2016.
- [38] K. X. Steirer, J. P. Chesin, N. E. Widjonarko et al., "Solution deposited NiO thin-films as hole transport layers in organic photovoltaics," *Organic Electronics*, vol. 11, no. 8, pp. 1414–1418, 2016.
- [39] G. A. Sepalage, S. Meyer, A. Pascoe et al., "Copper(I) iodide as hole-conductor in planar perovskite solar cells: probing the origin of *J* - *V* hysteresis," *Advanced Functional Materials*, vol. 25, no. 35, pp. 5650–5661, 2015.
- [40] W.-Y. Chen, L.-L. Deng, S.-M. Dai et al., "Low-cost solution-processed copper iodide as an alternative to PEDOT:PSS hole transport layer for efficient and stable inverted planar heterojunction perovskite solar cells," *Journal of Materials Chemistry A*, vol. 3, no. 38, pp. 19353–19359, 2015.
- [41] W. Sun, S. Ye, H. Rao et al., "Room-temperature and solution - processed copper iodide as the hole transport layer for inverted planar perovskite solar cells," *Nanoscale*, vol. 8, no. 35, pp. 15954–15960, 2016.
- [42] C. Chappaz-Gillot, S. Berson, R. Salazar et al., "Polymer solar cells with electrodeposited CuSCN nanowires as new efficient hole transporting layer," *Solar Energy Materials and Solar Cells*, vol. 120, pp. 163–167, 2014.
- [43] B. Li, L. Wang, B. Kang, P. Wang, and Y. Qiu, "Review of recent progress in solid-state dye-sensitized solar cells," *Solar Energy Materials and Solar Cells*, vol. 90, no. 5, pp. 549–574, 2006.
- [44] P. Pattanasattayavong, N. Yaacobi-Gross, K. Zhao et al., "Hole-transporting transistors and circuits based on the transparent inorganic semiconductor copper(I) thiocyanate (CuSCN) processed from solution at room temperature," *Advanced Materials*, vol. 25, no. 10, pp. 1504–1509, 2013.
- [45] P. Qin, S. Tanaka, S. Ito et al., "Inorganic hole conductor-based lead halide perovskite solar cells with 12.4% conversion efficiency," *Nature Communications*, vol. 5, article 3834, 2014.
- [46] S. Ye, S. W. Sun, Y. Li et al., "CuSCN-based inverted planar perovskite solar cell with an average PCE of 15.6%," *Nano Letters*, vol. 15, no. 6, pp. 3723–3728, 2015.
- [47] V. E. Madhavan, I. Zimmermann, C. Roldan-Carmona et al., "Copper thiocyanate inorganic hole-transporting material for high-efficiency perovskite solar cells," *ACS Energy Letters*, vol. 1, no. 6, pp. 1112–1117, 2016.
- [48] M. Jung, Y. C. Kim, N. J. Jeon et al., "Thermal stability of CuSCN hole conductor-based perovskite solar cells," *ChemSusChem Communications*, vol. 9, no. 18, pp. 2592–2596, 2016.
- [49] P. Pattanasattayavong, G. O. Ngongang Ndjawa, K. Zhao et al., "Electric field-induced hole transport in copper(I) thiocyanate (CuSCN) thin-films processed from solution at room temperature," *Chemical Communications*, vol. 49, no. 39, pp. 4154–4156, 2013.
- [50] B. K. Meyer, A. Polity, D. Reppin et al., "Binary copper oxide semiconductors: from materials towards devices," *Physica Status Solidi B*, vol. 249, no. 8, pp. 1487–1509, 2012.
- [51] L.-C. Chen, "Review of preparation and optoelectronic characteristics of Cu_2O -based solar cells with nanostructure," *Materials Science in Semiconductor Processing*, vol. 16, no. 5, pp. 1172–1185, 2013.
- [52] C. Zuo and L. Ding, "Solution-processed Cu_2O and CuO as hole transport materials for efficient perovskite solar cells," *Small*, vol. 11, no. 41, pp. 5528–5532, 2015.
- [53] F. Hou, Z. Su, F. Jin et al., "Efficient and stable planar heterojunction perovskite solar cells with an MoO_3 /PEDOT:PSS hole transporting layer," *Nanoscale*, vol. 7, no. 21, pp. 9427–9432, 2015.
- [54] P. Li, C. Liang, Y. Zhang, F. Li, Y. Song, and G. Shao, "Polyethyleneimine High-Energy Hydrophilic Surface Interfacial Treatment toward Efficient and Stable Perovskite Solar Cells," *ACS Applied Materials & Interfaces*, vol. 8, no. 47, pp. 32574–32580, 2016.
- [55] H. Sun, X. Hou, Q. Wei et al., "Low-temperature solution-processed p-type vanadium oxide for perovskite solar cells," *Chemical Communications*, vol. 52, no. 52, pp. 8099–8102, 2016.



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