



HOKKAIDO UNIVERSITY

Title	Optimization of nanoarchitectures for high-performance planar perovskite solar cells [an abstract of entire text]
Author(s)	Shalan, Ahmed Esmail Kamal
Description	この博士論文全文の閲覧方法については、以下のサイトをご参照ください。 https://www.lib.hokudai.ac.jp/dissertations/copy-guides/
Degree Grantor	北海道大学
Degree Name	博士(情報科学)
Dissertation Number	甲第12635号
Issue Date	2017-03-23
Doc URL	https://hdl.handle.net/2115/65849
Type	doctoral thesis
File Information	Ahmed_Esmail_Kamal_Shalan_summary.pdf



Ph. D. thesis (short summary)

Optimization of nanoarchitectures for high-performance planar perovskite solar cells

Ahmed Esmail Kamal Shalan

Graduate School of Information Science and Technology, Hokkaido University

Abstract

Perovskite solar cells (PSCs) based on organometal halide light-absorbing materials have attracted enormous research interest for solar cell applications due to their many intriguing optical and electronic features, such as large absorption coefficient, large charge-carrier mobility, long carrier-recombination lifetime and unique defect physics. Since the first report on a solid-state PSC with a (power conversion efficiency) PCE of 9.7% in 2012, and a PCE of 22.1% was certified in 2016. To improve the net PCE value more, it is important to elucidate the essential factors influencing on the PCE. This thesis focused on several element technologies to enhance PCE and the external quantum efficiency (EQE) from the viewpoints of 1) the light-harvesting, and 2) the hole extraction material. These studies were performed in order to give a better understanding and insight into the nanoarchitectures optimization for high-performance PSCs.

Although a lot of studies have been done related to PSCs, the EQE values are almost saturated especially in the longer wavelengths. Therefore, it is necessary to find a new way to improve the EQE at longer wavelengths for PSCs. Plasmonics is a highly promising due to its light-harvesting property. In this section, inverted planar PSCs with a p-i-n device configuration of indium-doped tin oxide (ITO)/NiO/CH₃NH₃PbI₃/[6,6]-phenyl-C₆₁-butanoic acid methyl ester (PCBM)/Ag with and without gold nanoislands (Au NIs) were prepared. The results demonstrated that the Au NIs increased the PCE to 5.1%, almost twice that of the samples without Au NIs. This result is due to the excitation of surface plasmons. Furthermore, we observed an enhancement of EQE at wavelengths shorter than the plasmon resonance. It is speculated that the plasmoelectric potential effect may contribute to the enhancement of EQE at the off-resonance region.

A hole-extracting layer (HEL) is a key material which affects device performances of PSCs. CoO_x is a promising HEL for inverted planar PSCs with a p-i-n device configuration of ITO/CoO_x/CH₃NH₃PbI₃/PCBM/Ag. The devices fabricated according to a simple solution procedure showed the best photovoltaic PCE 14.5%, which is significantly superior to those fabricated with traditional HEL such as PEDOT:PSS (12.2%), NiO_x (10.2%) and CuO_x (9.4%), under the same experimental conditions. Photoluminescence (PL) spectra and the corresponding PL lifetime of perovskite deposited on varied HEL films were measured to obtain the hole-extracting characteristics, for which the hole-extracting times consistent with the trend of their PCE. The reproducibility and endurance of those devices were examined to show the outstanding long-term stability of the devices made of metal oxide HEL, for which the CoO_x device still had PCE ~12% for over 1000 h.

Keywords: Localized surface plasmon, Perovskite solar cells, Nickel Oxide, Pulsed laser deposition, Cobalt oxide, Hole-extraction layer, Long-term stability.

Introduction

Perovskite (PSK) materials have many advantages, namely, an appropriate direct band gap, a high absorption coefficient, and propensity to make thin films with good carrier transport properties and an manifest tolerance of defects,^[1] has facilitated the fast increase in power conversion efficiencies (PCEs) of PSK solar cells (PSCs) from 3.8% to up to 20% within 6 years.^[2-4] To improve the net PCE value, it is important to elucidate the essential factors for the improvement of PCE. Here, we focus on several element technologies to enhance PCE and the external quantum efficiency (EQE) from the viewpoints of 1) the light-harvesting, and 2) the hole extraction material.

1) Plasmonic nanoparticles for the efficient light harvesting

Although many studies have been performed about PSCs, the EQE values are almost saturated especially in the longer wavelength region. Hence, it is necessary to find a new approach to increasing the EQE at longer wavelengths for small-grain-size PSK cells. Gold nanoislands (Au NIs) are considered to be a good candidate for operating as optical antennas, in which Au NIs strongly interact with the incident light and induce electromagnetic field enhancement and/or light scattering through localized surface plasmon resonance (LSPR).^[5] For the efficient charge separation in the PSK cell, the PSK layer should be thinner because the formed electron and hole have to migrate to the electron transport layer (ETL) and HEL, respectively. However, the light absorption efficiency should decrease, so that the thickness of PSK layer should be thin. On the other hand, plasmonically-enhanced near field promotes the excitation probability of PSK, which leads to make the PSK layer thinner. Especially, Au NIs should be placed near the HEL because the mobility of a hole in the PSK is substantially smaller than that of an electron.^[6,7] Therefore, we endeavor to deposit Au NIs in the interface between the NiO and the PSK. Even the longer wavelength light can be localized near the NiO/PSK interface, and light is absorbed by the PSK near the interface via LSPR. As an important point of this study, we deposited a NiO layer as the HEL with two different thicknesses on the ITO substrate by a pulsed laser deposition (PLD) system. We speculate on the mechanism how the free carriers (electrons and holes) path through the p-i-n planar PSCs in the absence and presence of Au NIs for the shorter and longer wavelengths, as shown in the schematic diagrams of Figure 1.

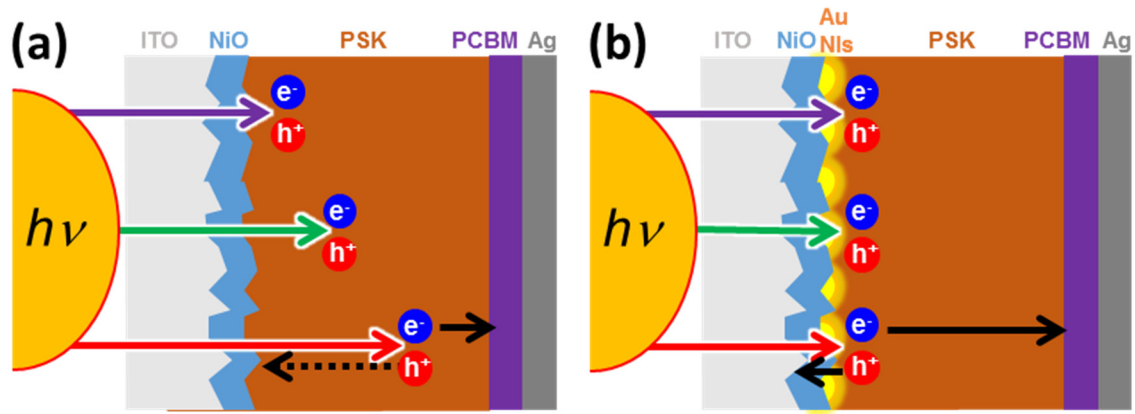


Figure 1. Schematics of the speculated mechanism of the free carrier (electrons and holes) pathway in the shorter and longer wavelengths in the absence (a) and presence (b) of Au NIs.

2) CoO_x as the efficient hole extraction material

Research on organic photovoltaic and light-emitting diode devices has already expounded that PEDOT:PSS is not suitable as the HEL in terms of the long-term stability of

the device due to its high acidity and hygroscopicity.^[8] Hence, many inorganic semiconductors, including MoO_x, NiO_x, V₂O₃, and WO₃,^[9] have been utilized to substitute PEDOT:PSS. In this study, we present the first demonstration of use of CoO_x as an efficient HEL for PSC applications: the ultrathin CoO_x film was prepared on an ITO substrate via spin-coating of the cobalt acetate tetrahydrate precursor solution to exhibit an effective surface coverage and great transparency in the visible region. The composition, crystallinity, morphology and surface roughness of the CoO_x films were examined via XPS, XRD, SEM and AFM techniques, respectively. As a result, the inverted PHJ PSC devices made of the CoO_x film as an efficient HEL exhibit the best PCE, 14.5 %, which outperforms those with the HEL made of PEDOT:PSS (12.2 %), NiO_x (10.2 %) and CuO_x (9.4 %). Photoluminescence (PL) spectra and transient PL decays of perovskite deposited on varied HEL films were recorded; the results show the hole-extraction times (τ_h) with order $\tau_h(\text{CoO}_x) < \tau_h(\text{PEDOT:PSS}) < \tau_h(\text{NiO}_x) < \tau_h(\text{CuO}_x)$; this order is consistent with the trend of their photovoltaic performances, indicating the superior hole-extracting characteristic of the CoO_x film as an efficient HEL responsible for the high-performance inverted planar perovskite solar cells reported herein.

Experimental

1) Plasmonic nanoparticles for the efficient light harvesting

To investigate the efficacy of Au NIs on inverted PHJ PSCs with NiO as the HEL, the solar cell devices were assembled in the presence of Au NIs. As shown in Figure. 2, it can be considered that the locations of the Au NIs loaded at the interface between the NiO and PSK layer may play an important role for the PCE by facilitating scattering of the light through LSPR.^[10]

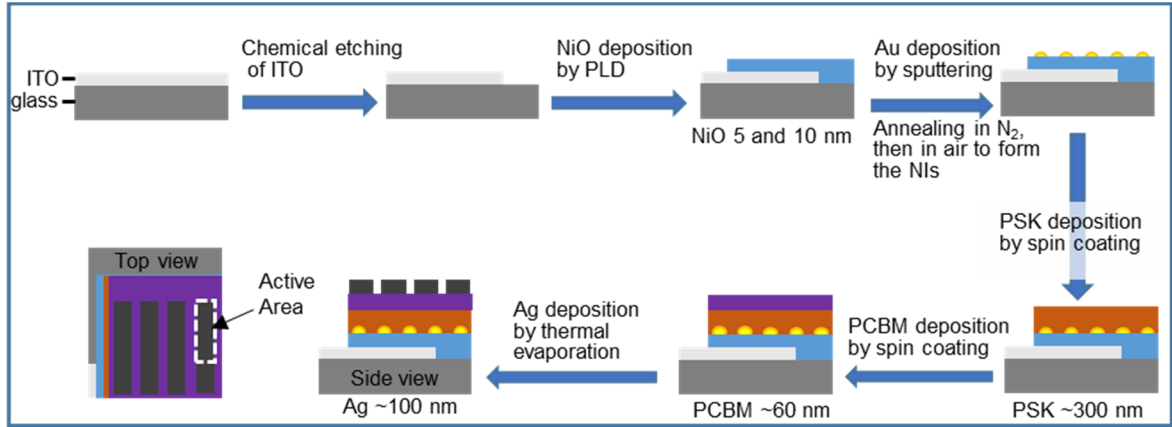


Figure 2. A schematic of the layer-by-layer fabrication process for the full-structure PSC with Au NIs with the configuration of glass/ITO/NiO/Au NIs/PSK/PCBM/Ag.

2) CoO_x as the efficient hole extraction material

A schematic diagram presented step by step in Figure 3 to show the preparation to fabricate our CoO_x device; the details are given in the experimental section. The right side of the scheme shows photographs of our device viewed from both sides.

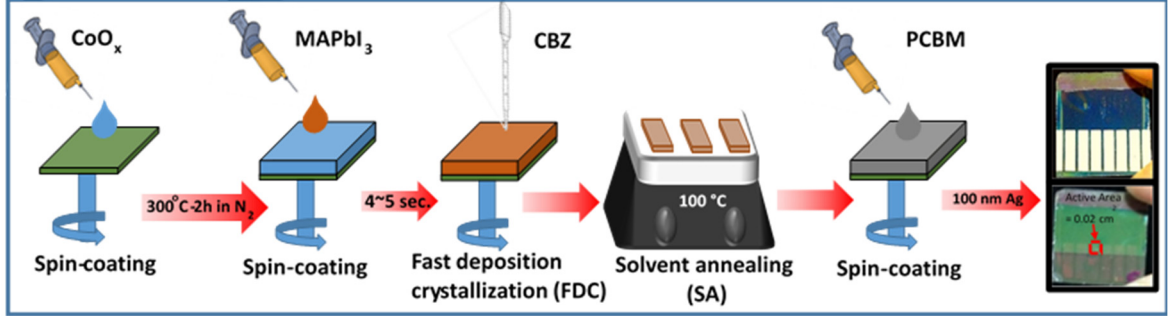


Figure 3. Schematic diagrams of preparation of an inverted planar perovskite solar cell.

Results and discussion

1) Plasmonic nanoparticles for the efficient light harvesting

In order to optimize the condition of the NiO ultrathin film, we first evaluate the PCEs using two different thicknesses. We pick out NiO with a thickness of 5 and 10 nm for comparison because it is predictable that the thinner NiO as the HEL shortens the path of the holes and prevents recombination between holes and electrons. However, the results show that when the NiO film is thicker, i.e., 10 nm, the cell obtained better photovoltaic performances as shown in Figure 4.

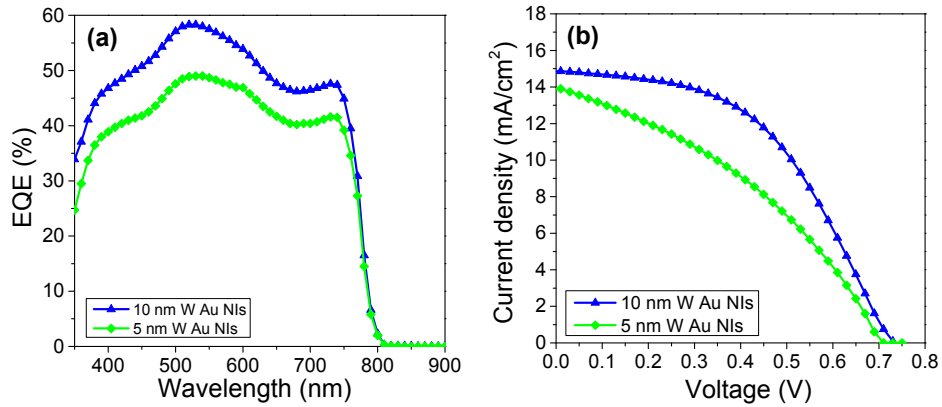


Figure 4. (a) EQE action spectra and (b) Device performance for NiO ultrathin films with thicknesses of 5 and 10 nm with Au NIs based on the device structure of ITO/NiO/PSK/PCBM/Ag.

J-V, IPCE, Δ IPCE and Δ extinction of NiO 10 nm with and without Au NIs

The EQE (Δ EQE) enhancement ratio of the 10-nm-thick NiO devices was calculated and emulate with their Δ extinction spectrum, as shown in Figure 5. The Δ extinction spectrum was founded from the difference between the extinction spectra of samples of 10-nm-thick NiO with and without Au NIs. It is noted around the band edge of the PSK that the EQE of the plasmonic device increases sharply. The extinction spectrum wavelength of the NiO/PSK cells with a thickness of 10 nm overlapped with the Δ EQE band in the region of wavelengths of greater than 650 nm, which is because of the electric field enhancement or the scattering effects of the Au NIs. Moreover, it is plainly founded that FF and the short-circuit current density (J_{sc}) are enhanced by the incorporation of Au NIs into the devices, which cause an increase in PCE.

Furthermore, from Figure 5, we note two peaks for Δ EQE. One of them is at longer wavelengths, which may be due to LSPR, localizing the light near the NiO/PSK interface, where light is absorbed by the PSK near the interface. The confirmation of this explanation done by the correlation between the Δ extinction spectrum and Δ EQE in the region of longer wavelengths. The other peak for Δ EQE founded at shorter wavelengths, which is not in agreement with LSPR and direct us to put in our mind another mechanism to explain this phenomenon in the next section.

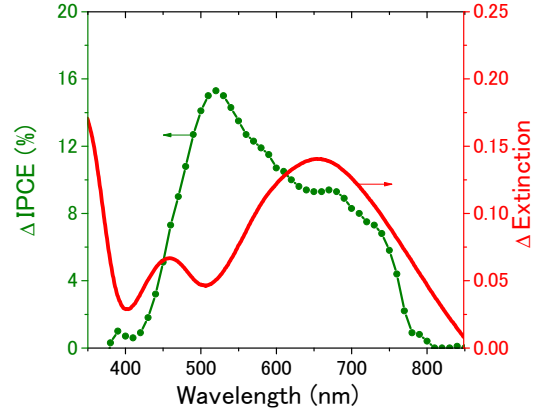


Figure 5. Comparison of the Δ EQE action spectrum of the PSCs and the Δ extinction between samples with and without Au NIs.

Plasmo-electric potential effect as a speculated mechanism for PSCs

Recently, the tuning of the plasmon resonance frequency of a nanostructure has been explained by modulating the electron density.^[11,12] The plasmonic resonance was shifted to higher or lower frequencies, respectively when a static electric potential was applied to inject or remove electrons from resonant structures. The electrical state of the conductor is coupled with the frequency of the plasmonic resonance. The reverse effect was demonstrated by Atwater et al.—the optical generation of an electrostatic potential due to an optically driven change in carrier density in a plasmonic nanostructure.^[13] They noticed that irradiation at wavelengths shorter and longer than the plasmon resonance peak created negative and positive surface potentials as a result of electron injection and ejection, respectively.

By applying this discovery to our results in the current work, we can speculate on the possible mechanism of EQE enhancement via plasmoelectric potential effects in the shorter wavelength region of LSPR. Two scenarios can be used to explain the mechanism: the electron is transferred from the NiO or from the PSK to the Au NIs under irradiation at wavelengths shorter than the plasmon resonance peak. In the former scenario, the valence band (VB) of the NiO shifts to positive values, and the open-circuit voltage (V_{oc}) values decrease. Simultaneously, the photocurrent increases as a result of efficient hole transport. In the latter scenario, at the interface between the Au NIs and the PSK separates the electron and hole the local electric field generated spatially.

2) CoO_x as the efficient hole extraction material

The performance of the PSCs through J-V and IPCE curves for CoO_x as HEL.

Figure 6a shows the current density–voltage (J–V) curves of devices of four types under AM 1.5 G one-sun irradiation. The CoO_x device exhibits $V_{oc}/V = 0.949$, $J_{sc}/mA\ cm^{-2} = 20.28\ mA\ cm^{-2}$, and fill factor $FF = 0.755$, corresponding to $PCE = 14.5\ %$, which is greater than that assembled using the traditional HEL PEDOT:PSS (12.2%), and is significantly greater than those of the other two metal-oxide-based HEL, NiO_x (10.2 %) and CuO_x (9.4 %), under the same experimental conditions. Figure 6b shows IPCE action spectra of the corresponding devices.

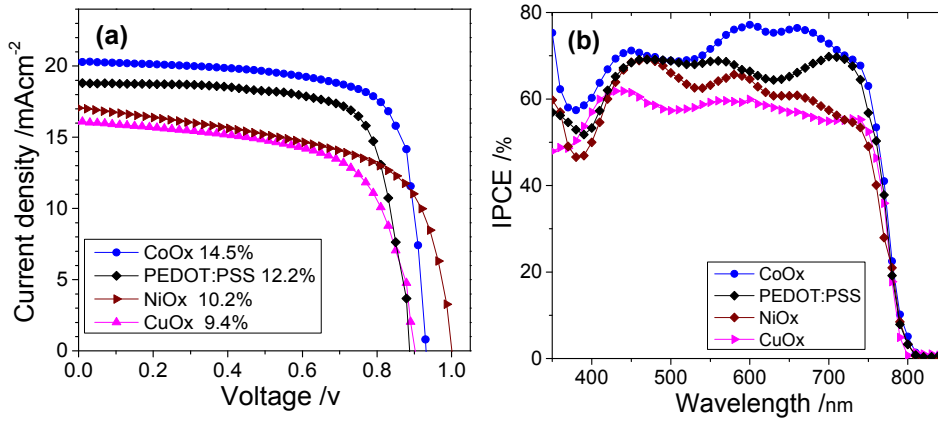


Figure 6. (a) Current-voltage curves and (b) IPCE of CoO_x, PEDOT:PSS, NiO_x and CuO_x devices as hole-extraction layers (HEL) as indicated.

Charge-extraction property of the HEL films.

To gain further insight into the charge-extraction property of the HEL films affecting their corresponding photovoltaic performances, we undertook time-resolved spectral measurements for perovskite deposited on varied HEL films investigated herein. First, we performed steady-state photoluminescence (PL) measurements to assess the effect of PL quenching of perovskite due to varied charge extraction of those PSK/HEL films. As the PL spectra show in Figure 7a, the PL intensity of PSK decreased significantly when the PSK layer was in contact with the HEL showing PL intensities with order CuO_x > NiO_x > PEDOT:PSS > CoO_x, indicating the hole-extracting ability in the reverse order, i.e., the CoO_x film should have the best hole-extracting ability due to the existence of an efficient non-radiative process to quench the PL effectively. To investigate further the kinetics of this efficient non-radiative process, we measured transient PL decay using the time-correlated single-photon-counting (TCSPC) technique with excitation at 635 nm and probe at 770 nm.

The PL transient profiles shown in Figure 7b are well fitted with a bi-exponential decay function.^[14] The average PL lifetimes (τ_{PL}) were determined with an intensity-averaged approach reported elsewhere. τ_{PL} for only MAPbI₃ deposited on ITO was determined to be 369.6 ns, but decreased to 2.8, 16.8, 21.6 and 136.7 ns when perovskite was in contact with the HEL of CoO_x, PEDOT:PSS, NiO_x and CuO_x, respectively. Assuming that hole extraction by the HEL is the most predominant non-radiative relaxation path, the interfacial hole extraction times (τ_h) in the MAPbI₃/HTM interface can be estimated to be 2.8, 17.5, 22.8 and 208.5 ns for HEL of CoO_x, PEDOT:PSS, NiO_x and CuO_x, respectively. Our results indicate that the hole-extraction time of the CoO_x layer is much shorter than those of the

other HEL, which reasonably explains the superior photovoltaic performance of the CoO_x device with greater J_{sc} and FF values than those of other devices.

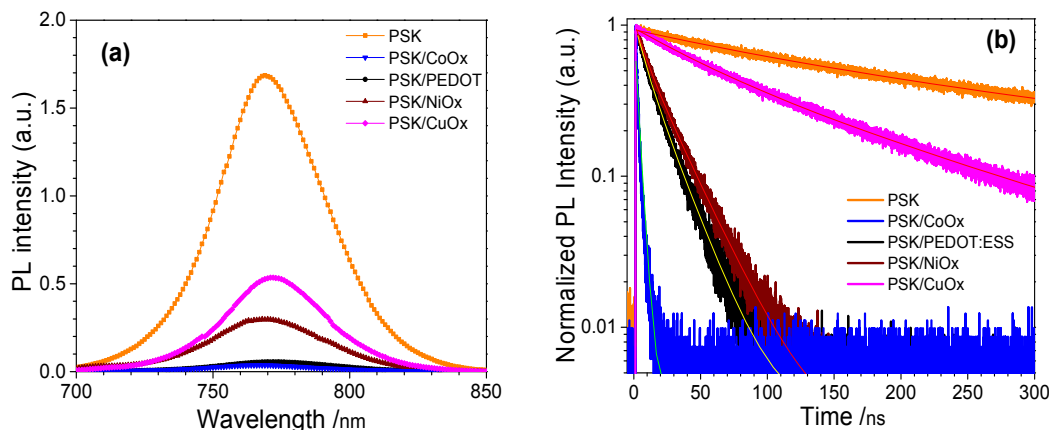


Figure 7. (a) Photoluminescence (PL) spectra and (b) PL decay profiles of MAPbI_3 (PSK), and PSK deposited on varied HEL films.

Performance reproducibility and stability of PSCs

The performance reproducibility of the devices was examined on fabricating 30 identical devices according to the same experimental procedure for each HEL film. Figure 8a shows histograms of the PCE distributions for devices made of these four HEL for comparison. Our results show that these devices were satisfactorily reproducible with average $\text{PCE} / \% = 12.4 \pm 0.7$, 11.5 ± 0.7 , 9.3 ± 0.5 and 8.3 ± 0.4 for devices made of CoO_x , PEDOT:PSS, NiO_x and CuO_x , respectively. To examine their long-term stability, we tested also the endurance of the devices of the four types kept in darkness and in glove box under a N_2 atmosphere; the corresponding stability results are shown in Figure 8b.

Even though the performance of the PEDOT:PSS device remained $\text{PCE} \sim 12\%$ in the first 100 h, it degraded rapidly after 100 h; the efficiency vanished after storage over 900 h. In contrast, all devices made of metal-oxide HEL (CoO_x , NiO_x and CuO_x) demonstrated great enduring stability over a period 43 days (more than 1000 h) and maintained $\sim 90\%$ of their initial efficiencies with the trend of performance showing the order $\text{CoO}_x > \text{NiO}_x > \text{CuO}_x$.^[14]

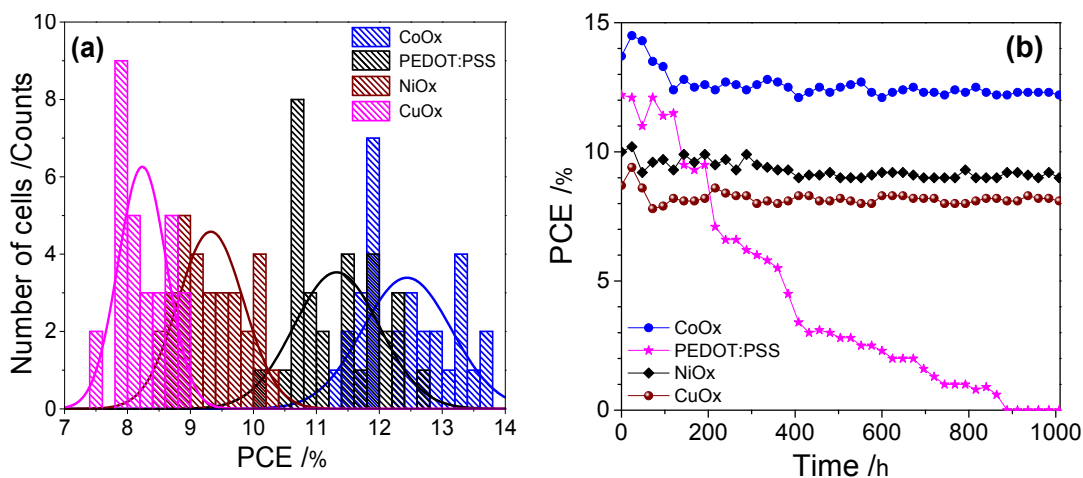


Figure 8. (a) PCE distribution histograms and (b) PCE vs. storage period for devices with HEL made of CoO_x , PEDOT:PSS, NiO_x and CuO_x as indicated.

Conclusions

Highly transparent, nanostructured NiO films with two different thicknesses were prepared through PLD. Furthermore, the PCE enhancement in PSCs was achieved by incorporating plasmonic Au NIs at the interface of the NiO and PSK. This enhancement could be attributed to the LSPR excitation in the range of 650–800 nm via strong scattering and improvement of the electric field in the nearness of the metal nanoparticle. Furthermore, a plasmoelectric potential effect is proposed as a possible mechanism of EQE enhancement in the shorter wavelength region of the LSPR peak. These results demonstrate that the location of NIs plays an important role in improving the charge extraction properties, and the PCEs of samples with Au NIs were 5.1%, which is almost double those values obtained with samples without Au NIs.

In another hand, a uniform and ultra-thin layer of CoO_x was prepared using a simple solution method. It used as an efficient HEL electrode for inverted planar hetero-junction perovskite solar cells. The PHJ devices were fabricated with CoO_x as HEL and the best photovoltaic performance attained PCE 14.5 %, which is superior to those of the devices with the HEL made of PEDOT:PSS, NiO_x and CuO_x under the same experimental conditions. The results of measurements of steady-state and time-resolved photoluminescence show hole-extraction rates with order CoO_x > PEDOT:PSS > NiO_x > CuO_x, which is matches with the trend of their corresponding photovoltaic performances in the same order.

References

- [1] Green, M. A.; Baillie, A. H.-; Snaith, H. J.; “The emergence of perovskite solar cells, *Nat. Photonics* **2014**, 8, 506–514.
- [2] Ball, J. M.; Lee, M. M.; Hey, A.; Snaith, H. J. “Low-temperature processed mesosuperstructured to thin-film perovskite solar cells,” *Energy Environ. Sci.*, **2013**, 6, 1739–1743.
- [3] Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J., Baker, R. H.-; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G.; “Lead Iodide Perovskite Sensitized All-Solid-State Submicron Thin Film Mesoscopic Solar Cell with Efficiency Exceeding 9%”, *Sci. Rep.*, **2012**, 2, 591–1–7.
- [4] Kojima, A.; Teshima, K.; Shirai, Y.; Miyasaka, T. “Organometal Halide Perovskites as Visible-Light Sensitizers for Photovoltaic Cells,” *J. Am. Chem. Soc.*, **2009**, 131, 6050–6051.
- [5] Lu, Z.; Pan, X.; Ma, Yingzhuang; Li, Y.; Zheng, L.; Zhang, D.; Xu, Q.; Chen, Z.; Wang, S.; Qu, B.; Liu, F.; Huang, Y.; Xiao, L.; Gong, Q., “Plasmonic-enhanced perovskite solar cells using alloy popcorn nanoparticles”, *RSC Advances*, **2015**, 5, 11175–11179.
- [6] Stranks, S. D.; Eperon, G. E.; Grancini, G.; Menelaou, C.; Alcocer, M. J. P.; Leijtens, T.; Herz, L. M.; Petrozza, A.; Snaith, H. J., “Electron-Hole Diffusion Lengths Exceeding 1 Micrometer in an Organometal Trihalide Perovskite Absorber”, *Science*, **2013**, 342, 341–344.
- [7] Xing, G.; Mathews, N.; Sun, S.; Lim, S. S.; Lam, Y. M.; Grätzel, M.; Mhaisalkar, S.; Sum, T. C., “Long-Range Balanced Electron- and Hole-Transport Lengths in Organic-Inorganic CH₃NH₃PbI₃”, *Science*, **2013**, 342, 344–347.
- [8] Taame A B.; Wei-N. S.; Ching-H. C.; Chun-J. P.; Ju-H. C.; Hung-M. C.; Meng-C. T.; Liang-Y. C.; Amare A. D.; Bing-J. H.; Organometal halide perovskite solar cells: degradation and stability. *Energy Environ. Sci.* **2016**, 9, 323–356.
- [9] Subbiah, A. S.; Halder, A.; Ghosh, S.; Mahuli, N.; Hodes, G.; Sarkar, S. K. Inorganic Hole Conducting Layers for Perovskite-Based Solar Cells. *J. Phys. Chem. Lett.* **2014**, 5, 1748–1753.

- [10] Shalan, A. E.; Oshikiri, T.; Sawayanagi, H.; Nakamura, K.; Ueno, K.; Sun, Q.; Wu, H.-P.; Diau, E. W.; Misawa, H., “Versatile Plasmonic-Effects at the Interface of Inverted Perovskite Solar Cells”, *Nanoscale*, **2017**, *9*, 1229–1236.
- [11] Polman, A., “Plasmonics Applied”, *Science*, **2008**, *322*, 868–869.
- [12] Novo, C.; Funston, A. M.; Gooding, A. K.; Mulvaney, P., “Electrochemical Charging of Single Gold Nanorods”, *J. Am. Chem. Soc.*, **2009**, *131*, 14664–14666.
- [13] M. T. Sheldon, J. van de Groep, A. M. Brown, A. Polman, H.; A. Atwater, “Nanophotonics. Plasmoelectric Potentials in Metal Nanostructures”, *Science*, **2014**, *346*, 828–831.
- [14] Shalan, A. E.; Oshikiri, T.; Narra, S.; Elshanawany, M. M.; Ueno, K.; Wu, H.-P.; Nakamura, K.; Shi, X.; Diau, E. W.; Misawa, H., “Cobalt Oxide (CoO_x) as an Efficient Hole-extracting Layer for High-performance Inverted Planar Perovskite Solar Cells”, *ACS Appl. Mater. Interfaces* **2016**, *8*, 33592–33600.