

# Surface-reconstruction of NiO<sub>x</sub> nanocrystals makes a breakthrough in flexible solar cells

Hong Zhang<sup>1,2,\*</sup> and Wallace C.H. Choy<sup>1,\*</sup>

**Lightweight flexible perovskite solar cells are promising for building-/vehicle-integrated photovoltaics, wearable electronics, and aerospace applications. Recently in *Nature Energy*, Li et al. reconstruct the surface properties of low-temperature processed NiO<sub>x</sub> nanocrystal film by tailoring a self-assembled monolayer. A record power conversion efficiency of 24.4% (certified) was achieved in flexible solar cells using an all-perovskite tandem structure.**

Lightweight flexible solar cells have attracted intensive attention because of their various promising applications in building-/vehicle-integrated photovoltaics, wearable electronics, portable energy systems and aerospace applications. Since the first demonstrated application in photovoltaics in 2009,<sup>1</sup> metal halide perovskites have been widely regarded as the emerging light-harvesting materials for next-generation thin-film solar cells due to the merits of their low-cost, high absorption coefficient, solution processability, long electron-hole diffusion length, and so on. Their high absorption coefficient enables the active layer of the device to be very thin with a thickness of ~500 nm to absorb the entire visible solar spectrum. Combined, these features result in the capability to realize low-cost, high-efficiency, and lightweight flexible solar cells.

The power conversion efficiency (PCE) of flexible perovskite solar cells (PSCs) have rapidly improved to over 21% (highest certified of 19.9%) within a decade.<sup>2</sup> Recently, there is an increasing global effort to advance flexible PSCs, and much of these endeavors are focused on the development of new composition, carrier transporting materials, interfacial engineering, and processing methods. In particular, non-stoichiometric nickel oxide (NiO<sub>x</sub>) nanocrystals developed by our group<sup>3,4</sup> have been

extensively studied as a low-cost and highly efficient hole-transporting material in flexible PSCs due to their robust chemical stability, low-temperature processability, high optical transmittance, and low fabrication costs. However, high trap densities and energy-level misalignment at the NiO<sub>x</sub>/perovskite interface constrain performance and operational stability of flexible PSCs.<sup>5</sup> Surface passivation of NiO<sub>x</sub> nanocrystal film with small molecules,<sup>6</sup> polymers,<sup>7</sup> ionic liquids,<sup>8</sup> and organic cations<sup>5</sup> led to the best PCE of ~20%<sup>9</sup> for *p-i-n* flexible PSCs. Therefore, modifying the surface properties of NiO<sub>x</sub> nanocrystal film with tailored molecules is an effective strategy to minimize the PCE difference between PSCs fabricated on rigid and flexible substrates.

Writing in *Nature Energy*, Li et al.<sup>10</sup> report a molecule-bridged hole-selective contact to mitigate interfacial recombination and facilitate hole extraction in flexible PSCs by anchoring hole-selective self-assembled monolayer (SAM) on the low temperature-processed NiO<sub>x</sub> nanocrystal film (Figure 1A). Considering the excellent hole selectivity and effective chemical bonding formation, two types of molecule, namely 2PACz ([2-(9H-carbazol-9-yl)ethyl] phosphonic acid) and MeO-2PACz ([2-(3,6-dimethoxy-9H-carbazol-9-yl)ethyl]phosphonic acid),

were selected for this study. The 2PACz and MeO-2PACz molecules anchor on the surface of NiO<sub>x</sub> via the phosphonic acid group, as evidenced by X-ray photoelectron spectroscopy and ultraviolet photoelectron spectroscopy measurements. In the meantime, the oxygen from the phosphoryl of the 2PACz passivates the defects in the buried interface of perovskite films via forming the Pb–O chemical bonding, as confirmed from the first-principle calculations. The anchoring of 2PACz and MeO-2PACz with different molecular dipole moments (2.0 debye versus 0.2 debye) is also capable to tune the energy-level alignment between NiO<sub>x</sub> and perovskites. As a result, the interfacial non-radiative recombination is suppressed at the interface between NiO<sub>x</sub> and perovskite absorber, which contributes to the improved photovoltaic performance of flexible single-junction PSCs. Furthermore, this strategy can be employed to fabricate flexible all-perovskite tandem solar cells with a certified PCE of 24.4% for device area of 0.049 cm<sup>2</sup>, which represents the highest performance among all types of flexible thin-film solar cells reported to date (Figure 1B). Meanwhile, surface-reconstruction of NiO<sub>x</sub> nanocrystals with hole-selective molecules improves the mechanical and operational stability of flexible PSCs.

This report opens a new way to fabricate flexible solar cells with high efficiency and stability for the broad applications. However, the mechanism is still not very clear for the self-assembly of the 2PACz and MeO-2PACz mixtures on the surface of NiO<sub>x</sub> nanocrystals. Meanwhile, the molecules used are still

<sup>1</sup>Department of Electrical and Electronic Engineering, The University of Hong Kong, Pokfulam Road, Hong Kong, P.R. China

<sup>2</sup>Institute of Optoelectronics, Fudan University, Shanghai 200433, P.R. China

\*Correspondence:  
hzhangjoe@fudan.edu.cn (H.Z.),  
chchoy@eee.hku.hk (W.C.H.C.)

<https://doi.org/10.1016/j.joule.2022.07.006>



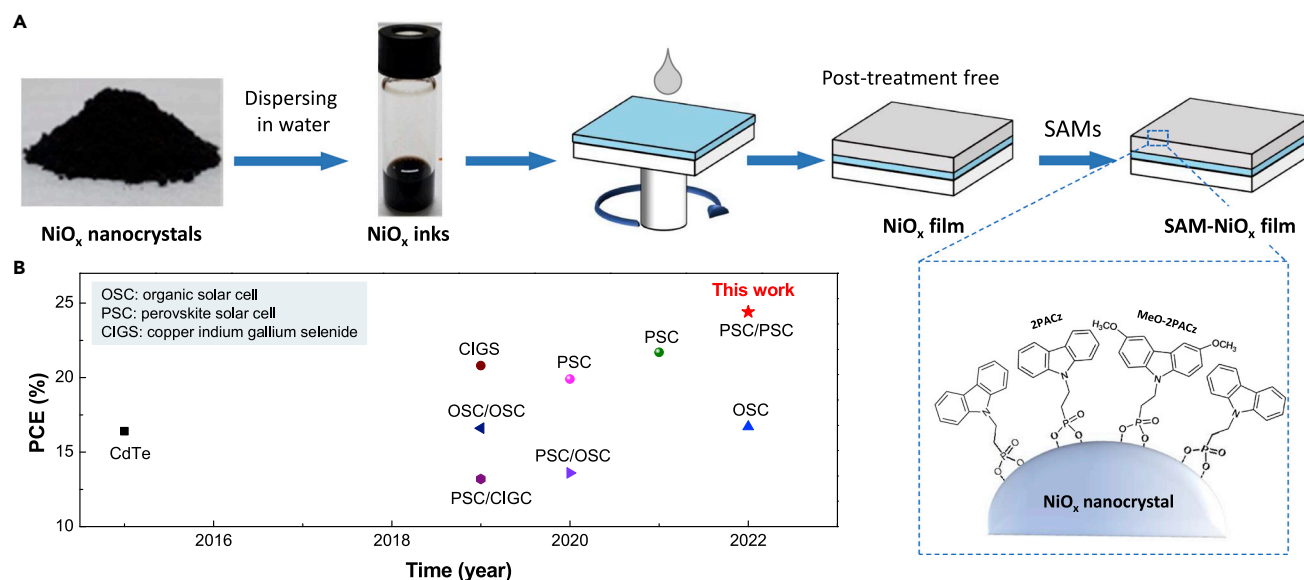


**Figure 1. Preparation of SAM-NiO<sub>x</sub> nanocrystal film and performance comparison of different types of flexible solar cells**

(A) Scheme of the SAM-NiO<sub>x</sub> nanocrystal film formation and the surface-reconstruction of NiO<sub>x</sub> nanocrystals with SAMs.

(B) Comparison of the flexible all-perovskite tandem prepared on SAM-NiO<sub>x</sub> substrate with other types of flexible solar cells.

very expensive and may increase the fabrication cost of flexible PSCs. In the near future, more insightful studies should focus on design guideline for developing more efficient and cheaper self-assembled molecules for large-scale manufacturing of lightweight flexible solar cells. Toward the practical applications of flexible PSCs, the mechanical and operational stabilities need to be further improved by a combination of interface engineering, material innovation of each functional layer, and encapsulation techniques.

## REFERENCES

- Kojima, A., Teshima, K., Shirai, Y., and Miyasaka, T. (2009). Organometal halide perovskites as visible-light sensitizers for photovoltaic cells. *J. Am. Chem. Soc.* 131, 6050–6051.
- Palmstrom, A.F., Eperon, G.E., Leijtens, T., Prasanna, R., Habisreutinger, S.N., Nemeth, W., Gaubling, E.A., Dunfield, S.P., Reese, M., Nanayakkara, S., et al. (2019). Enabling flexible all-perovskite tandem solar cells. *Joule* 3, 2193–2204.
- Zhang, H., Cheng, J., Lin, F., He, H., Mao, J., Wong, K.S., Jen, A.K.Y., and Choy, W.C.H. (2016). Pinhole-free and surface-nanostructured niox film by room-temperature solution process for high-performance flexible perovskite solar cells with good stability and reproducibility. *ACS Nano* 10, 1503–1511.
- Jiang, F., Choy, W.C.H., Li, X., Zhang, D., and Cheng, J. (2015). Post-treatment-free solution-processed non-stoichiometric niox nanoparticles for efficient hole-transport layers of organic optoelectronic devices. *Adv. Mater.* 27, 2930–2937.
- Boyd, C.C., Shallcross, R.C., Moot, T., Kerner, R., Bertoluzzi, L., Onno, A., Kavadiya, S., Chosy, C., Wolf, E.J., Werner, J., et al. (2020). Overcoming redox reactions at perovskite-nickel oxide interfaces to boost voltages in perovskite solar cells. *Joule* 4, 1759–1775.
- Wang, Q., Chueh, C.-C., Zhao, T., Cheng, J., Eslamian, M., Choy, W.C.H., and Jen, A.K.-Y. (2017). Effects of self-assembled monolayer modification of nickel oxide nanoparticles layer on the performance and application of inverted perovskite solar cells. *ChemSusChem* 10, 3794–3803.
- Du, Y., Xin, C., Huang, W., Shi, B., Ding, Y., Wei, C., Zhao, Y., Li, Y., and Zhang, X. (2018). Polymeric surface modification of niox-based inverted planar perovskite solar cells with enhanced performance. *ACS Sustain. Chem. Eng.* 6, 16806–16812.
- Zhang, S., Wang, H., Duan, X., Rao, L., Gong, C., Fan, B., Xing, Z., Meng, X., Xie, B., and Hu, X. (2021). Printable and homogeneous NiOx hole transport layers prepared by a polymer-network gel method for large-area and flexible perovskite solar cells. *Adv. Funct. Mater.* 31, 2106495.
- Ru, P., Bi, E., Zhang, Y., Wang, Y., Kong, W., Sha, Y., Tang, W., Zhang, P., Wu, Y., Chen, W., et al. (2020). High electron affinity enables fast hole extraction for efficient flexible inverted perovskite solar cells. *Adv. Energy Mater.* 10, 1903487.
- Li, L., Wang, Y., Wang, X., Lin, R., Luo, X., Liu, Z., Zhou, K., Xiong, S., Bao, Q., Chen, G., et al. (2022). Flexible all-perovskite tandem solar cells approaching 25% efficiency with molecule-bridged hole-selective contact. *Nat. Energy*. <https://doi.org/10.1038/s41560-022-01045-2>.