

The Impact Of Ligand Engineering On Low Temperature NiO Hole Transporting Materials For Perovskite Solar Cells

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Perovskite solar cells (PSCs) have recently reached over 25% in power conversion efficiency and are emerging as a promising competitor to silicon technology. The key challenge that remains in further developing of the PSCs is their scaling towards commercial fabrication. To achieve this, fully printed perovskite solar cells are still a major goal for the solar industry. As perovskites are inherently temperature sensitive, a key requirement for the realisation of these printed devices is the development of low-temperature processed layers that can form the individual components of a solar cell device. Hole transporting layers among the entire device structure are the most problematic materials, where the conventional spiro-MeOTAD, a doped organic molecule, is too expensive and unstable for commercial applications. Contrarily, inorganic nanomaterials can overcome the limitations of organic HTLs. Nickel oxide has been widely used as an HTL in perovskite solar cells, both through sputtered [1] [2] and solution-processed approaches [3]. However, these studies have indicated that it is a material that typically needs high temperature processing to ensure a sufficient crystallinity as to be useful as an HTL. Moreover, its performance within such devices has been inherently linked to its stoichiometry and surface structure [4]. The application of NiO in inverted PSCs has now also yielded high efficiencies (Fig. 1). The most commonly investigated devices have been fabricated with methylammonium lead iodide (MAPbI₃) light-absorbing layers, although the introduction of caesium-doped, mixed cation and halide perovskites [1, 5] have yielded the highest reported PCEs, at over 20%.

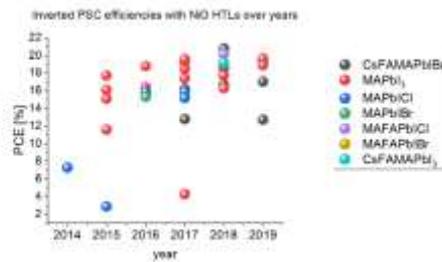


Fig. 1 Recent increase of power conversion efficiencies of nickel oxide-based solar cells with various types of perovskites.

For nickel oxide the processing temperatures of such films is typically $>250\text{ }^{\circ}\text{C}$ to achieve sufficient crystallinity for use in solar cells. The only way to omit high-temperature post-deposition annealing of solution-processed NiO HTLs is by spin-coating dispersion already containing metal oxide particles. Mild and quick heating can be then introduced to simply enhance the solvent drying at temperatures $<200\text{ }^{\circ}\text{C}$. However, for highly efficient perovskite solar cells additional interface engineering also needs to be studied in order to facilitate the charge transfer. Interestingly, surface properties and ligand engineering approaches have been comprehensively investigated on a wide range of nanoparticles, yet these research outcomes are not sufficiently applied in perovskite devices. Our motivation in the presented work is to fabricate NiO nanoparticle-based HTL inks for low temperature deposition, dedicated for perovskite solar cells. To achieve this goal, we have successfully synthesized fine NiO nanoparticles (of around 4 nm size, Fig. 2) via heat-up approach with assistance of oleic acid as capping agent and sodium oleate acting as a protective ligand [6].

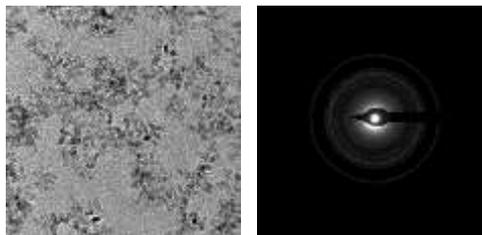


Fig. 2 TEM image and diffraction pattern of NiO nanoparticles synthesised via heat-up synthetic route.

The as-obtained NiO NPs are dispersible in nonpolar solvents, like hexane or toluene, due to oleate ligands present at their surface. However, these long alkyl chain ligands are not favourable for efficient charge transfer in the HTL. For that reason, our second aim was to apply different ligand modification procedures to improve the hole transfer within the device after removal of long alkyl ligands, and also, to investigate how the introduced ligands impact the charge extraction at the perovskite/HTL interface. The Figure 3 presents a schematic process of NiO film formation before and after the ligand exchange.

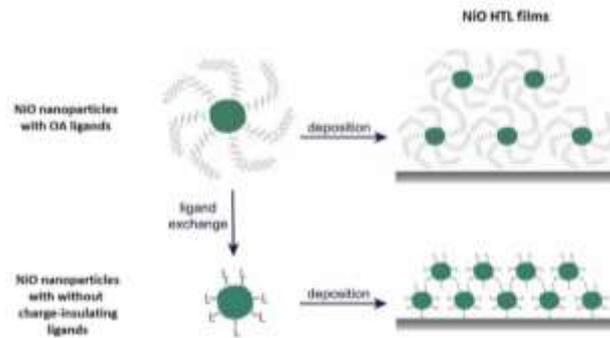


Fig. 3 Formation of NiO thin films with oleic acid ligands or exchanged ligands.

Two different ligand exchange routes were successfully applied, and for the very first time, deposited as NiO HTLs. In the first procedure, a Meerwein's salt Me_3OBF_4 , was used. The resulting NiO nanoparticles, stabilized by BF_4^- ligands, are dispersible in highly polar solvents, like dimethylformamide (DMF). The second procedure involved a hydroxybenzoic acid (HBA), and the as-modified nanoparticles are dispersible in polar solvents, like isopropanol (IPA).

To assess the performance of the synthesized and modified NiO HTLs we have fabricated perovskite solar cell of the inverted architecture (Fig. 4), with PCBM as the electron transporting layer and finished with silver electrodes. The standard NiO films were spin-coated from a toluene dispersion, whereas the Me_3OBF_4 -modified and HBA-modified were processed from DMF and IPA inks, respectively. All of the HTL films were annealed at a low temperature of just 140°C for 5 minutes to remove the residual solvent from the surface. Such processing parameters are in line with printing regime, especially on flexible substrates, which is an additional advantage of the developed materials.

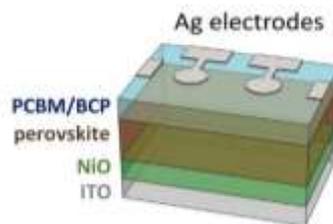


Fig. 4 The structure of the perovskite solar cells investigated in the presented work.

Both ligand-modified NiO HTLs exhibited higher power conversion efficiencies comparing to devices with standard, unmodified NiO charge transporting layers. Interestingly, the samples with hydroxybenzoate ligands presented higher stability than BF_4^- -modified metal oxide nanoparticles. This could be attributed to better passivation of the perovskite surface by the hydroxybenzoate ligands, and also, improved charge transfer facilitated by aromatic rings.

In summary, in our work we have successfully fabricated perovskite solar cells with NiO-based hole transporting layers before and after ligand exchange. All of the materials were processed

under mild conditions (<140 °C) which is the limit for printing technique, being one of the best approaches for fabrication of commercial products. The exchange of long alkyl chained ligands resulted in improvement of PSC performance and high stability of the devices. The outcomes of the presented study are highly promising for commercialization of perovskite-based photovoltaic devices.

References:

1. David P. McMeekin, e.a., *A mixed-cation lead mixed-halide perovskite absorber for tandem solar cells*. *Science*, 2016. **351**(6269): p. 151-155.
2. Xin Yan, e.a., *Optimization of sputtering NiOx films for perovskite solar cell applications*. *Materials Research Bulletin*, 2018. **103**: p. 150-157.
3. Jinjin He, e.a., *Ligand-Free, Highly Dispersed NiOx Nanocrystal for Efficient, Stable, Low-Temperature Processable Perovskite Solar Cells*. *Sol. RRL*, 2018. **2**(4).
4. G. Li, e.a., *Overcoming the Limitations of Sputtered Nickel Oxide for High-Efficiency and Large-Area Perovskite Solar Cells*. *Adv. Sci.*, 2017. **4**.
5. M. Saliba, e.a., *Cesium-containing triple cation perovskite solar cells: improved stability, reproducibility and high efficiency*. *Energy Environ. Sci.*, 2016. **9**: p. 1989-1997.
6. Xiaoyong Liang, e.a., *Synthesis of Unstable Colloidal Inorganic Nanocrystals through the Introduction of a Protecting Ligand*. *Nano Lett.*, 2014. **14**: p. 3117–3123.