APPLICATION OF DOPANT-FREE HOLE TRANSPORT MATERIALS FOR PEROVSKITE SOLAR CELLS

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In this work we present the synthesis, characterization and application of a series of additive and dopant free hole transport materials (HTM) for solid-state perovskite-based solar cells. Newly synthesized HTMs showed strong absorption in the visible spectral range and suitable HOMO-LUMO energy levels for the application for methylammonium lead(II) iodide ($CH_3NH_3PbI_3$) perovskite. Dopant-free perovskite solar cells have been fabricated using $CH_3NH_3PbI_3$ perovskite and the newly synthesized HTMs following sequential deposition method, which allows us to reach power conversion efficiencies as high as 11.4 %. The easy of synthesis, low cost and relatively high performance of newly synthesized HTMs has great prospects for commercial applications in the near-future.

Introduction

Nowadays, organic–inorganic metal trihalide perovskites [1] have received considerable attention in solid-state photovoltaics due to their interesting features such as, broad and strong absorption over the visible to near infrared region of the solar spectrum, high charge carrier mobilities reaching tens of square centimeters per voltsecond, large free charge recombination lifetimes on a timescale of hundreds of nanoseconds causing long carrier diffusion length, and small exciton binding energy [2].

Miyasaka and co-workers were the first to report the incorporation of perovskite as sensitizer in liquid electrolyte-based dye-sensitized solar cells, at that time allowing to reach power conversion efficiencies (PCE) of 3.8% [3]. Since then, extensive optimization of the metal oxide scaffolds, efficient device processing and fabrication conditions of the perovskite layer have been performed, thereby enabling to improve a PCEs to a certified value of 20.1 percent [4]. In most cases in these solar cell devices convenient 2,2',7,7'-tetrakis(*N,N*-di-*p*-methoxyphenylamino)-9,9'-spirobifluorene (spiro-MeOTAD) is used as hole transporting material, which due to its low conductivity also comprises various dopants and additives [5].

Although PCEs up to 10.6% were reported for HTM-free perovskite devices, the most efficient solar cells usually employed organic HTMs which play a key role for the hole transport and reduced charge recombination processes. In this respect, a wide range of materials have been developed as alternating organic HTMs showing excellent PCEs in the range from 10-16% but again using various additives and dopants [6, 7]. All these HTMs have no absorption in the visible to near-infrared region thus, acting only as hole transporter while perovskite functions as light absorber. Several low band gap polymeric semiconductors have also been tested in perovskite devices showing PCEs in the range from 5-9%. Despite of having significant absorption in the visible region these polymers do not contribute to the photo-current generation and function only as hole conductor.

Experimental

A mesoscopic perovskite solar cells sensitized by using methylammonium lead halides were fabricated after applying slightly modified sequential deposition technique [8]. Devices were prepared on conductive FTO coated glass substrates. A stock solution of lead iodide (PbI2) (in DMSO) were spin coated on the top of mesoporous TiO_2 layer which was formed by spin-coating and heating 30 nm sized titanium oxide nanoparticles. On the top of a led salt CH_3NH_3I in ethanol solution was sprayed and left for 20 s before spin coating at 3000 r.p.m. for 30 s.

Afterwards different types of HTMs were spin coated on the top of perovskite layer. Devices were finally completed by thermally evaporating 60-70 nm thick gold layer on the top of the HTM. The J-V characteristics of devices were measured while recording the current output using a digital source meter (Keithley Model 2400). The light source was a 450 W Xenon lamp (Oriel). The internal photon to current conversion efficiency (IPCE) of the devices was measured by focusing light from the 300W Xenon lamp (ILC Technology, U.S.A.) through a Gemini-180 double monochromator (Jobin Yvon Ltd., U.K.) while chopping at 3 Hz before illuminating onto the photovoltaic cell. Optical absorption spectra of all investigated materials were recorded with a CARY-5 UV-Vis-Nir spectrophotometer in transmission mode within the 500-850 nm range. Photoluminescence measurements were performed on spectrofluorometer Fluorolog 322 (Horiba Jobin Yvon Ltd). For solution measurements hole transporting materials were dissolved in tetrachloroethane at concentration of about 0.05 mM and measured in 10 mm path length quartz cuvette. While for films, HTM were spin coated on the top of amorphous glass, TiO_2 and perovskite.

Results and Discussion

Here we present the application of acceptor-donor-acceptor type, low band gap hole transport materials (HTM) for solid-state methylammoium lead iodide perovskite-based solar cells. The absorption spectra of perovskite films comprising hole transporting and hole-free layers are shown in Figure

1. The obtained optical absorption spectrum of the pristine methylammonium lead iodide perovskite film (represented by a solid black line) shows broad absorption band overreaching entire visible spectral range with band edge at around 780 nm. Large extinction coefficient and typical spectral behavior of methylammonium lead iodide perovskite film is consistent with that reported previously [9, 10]. The cells covered with hole transporting materials shows significant different absorption profiles. In the presence of HTMs the absorption band of perovskite films is strongly enhanced specifically in the spectral region beyond 550 nm, further supporting the contribution of possible light absorption of the HTMs.

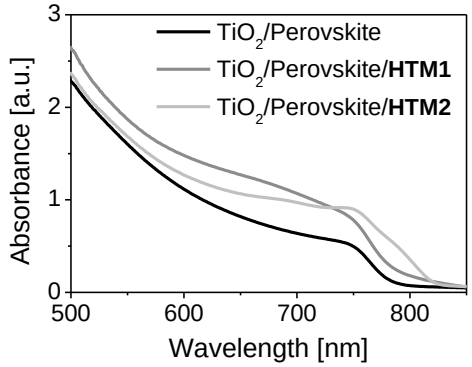

Fig. 1. Absorption spectra of TiO_2/perovskite films with and without HTMs.

Current voltage characteristics of three different devices with different composition are shown in Figure 2. The black line shows the *I-V* of the solar cell made from pristine perovskite with the composition: FTO/compact-TiO_2/mesoporous-TiO_2/$CH_3NH_3PbI_3$/Ag. The violet and green lines correspond to the devices with CS1 and CS2 hole transporting materials respectively. The photovoltaics parameters of complete devices are summarized in Table 1. As it can be seen, the power conversion efficiency for the reference cell is 7.1%, while it increases to 10.25% using CS2 and up to 11.4% using CS1 oligomers as HTM. The resulting increase of power conversion efficiency is determined by the increase of all three photovoltaic parameters.

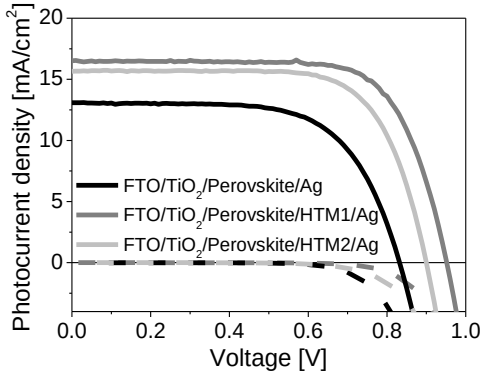

Fig. 2. Current voltage characteristics of the perovskite solar cells with and without hole transport layers.

The incident photon to electron conversion efficiency (IPCE) of photovoltaic perovskite devices with and without hole transporting materials are presented in Figure 3. As it could be seen, the overall conversion efficiency of the devices with hole transport materials is larger compared to the reference device comprising no HTM. Moreover, due to their broader absorption, these HTMs also contributed in the overallphotocurrent generation.

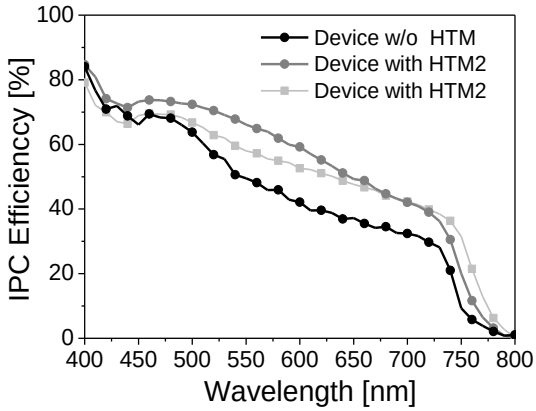

Fig. 3. The incident photon to current conversion efficiencies of perovskite solar cells with and without hole transport layers.

Conclusions

In summary, we have reported two new low band gap hole transporting materials suitable for application in $CH_3NH_3PbI_3$ perovskite solar cells allowing reaching power conversion efficiencies as high as 11.4% and 10.3%, respectively. It is worth mentioning that the high performance of these devices was achievable even without the use of any additive and dopant.

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