

Perovskite solar cells stabilized by carbon nanostructure-P3HT blends

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In the last five years, perovskite materials were introduced as light absorbers in solar cell devices with power conversion efficiency (η) up to 20.1% (certified) [1]. This very high η is related to the excellent optoelectronic properties of this material such as: direct band gap, broad absorption spectra, and high mobility of charge carriers [2]. The typical perovskite solar cells (PSCs) are fabricated using compact and mesoporous TiO₂ as electron transporting layer and 2,20,7,70-tetrakis-(N,N-di-*p*-methoxyphenylamine) 9,90-spirobifluorene (Spiro-OMeTAD) as the hole transporting material (HTL) [3]. In order to reduce the costs of PSC technology, conjugated polymers such as poly(3-hexylthiophene) (P3HT) have been proposed as a cheaper alternative to Spiro-OMeTAD for both small and large area devices. Here, we report our recent work, demonstrating that carbon nanostructures (CNSs) such as organic functionalized single-wall carbon nanotubes (SWCNTs) and graphene nanoplatelets (GNPs), derived from reduced graphene oxide, can act as conductive nanofillers in a P3HT layer used as HTL for hybrid PSCs based on CH₃NH₃PbI₃, thus providing better performances and longer time stabilities to devices [4].

4-Methoxyphenyl substituents were selected to be covalently bound on the surface of CNSs in order to allow their efficient dispersion in the semiconducting polymer matrix. The functionalization reaction was carried out by generating *in situ* the diazonium salt of 4-methoxyaniline in the presence of isopentylnitrite, using 1-cyclohexyl-2-pyrrolidone (CHP) as the solvent, thus obtaining 4-methoxyphenyl functionalized SWCNTs (**SWCNT-PhOMe**) and GNPs (**GNP-PhOMe**) (Figure 1) [5]. The effective incorporation of the functionalized CNSs into the P3HT matrix has been achieved by applying a thorough protocol of ultrasonication/centrifugation steps. Sedimentation-based separation [6] permitted us to eliminate insoluble residues, such as GNP aggregates and SWCNT bundles. Three different weight percentages of functionalized CNSs with respect to P3HT were prepared for each CNS type (namely 1%, 2% and 3% for the SWCNT-PhOMe/P3HT blend and 1%, 2% and 4% for the GNP-PhOMe/P3HT blend) by diluting the first blend solution obtained after ultrasonication/centrifugation/supernatant separation with a P3HT only solution.

Figure 2 reports the η under shelf-life test of PSCs fabricated with different doping percentages of 4-methoxyphenyl functionalized CNSs in P3HT as HTL. The PSCs based on SWCNT-PhOMe/P3HT blends as HTLs have shown higher η (V_{oc} = 863 mV, J_{sc} = 22.9 mA/cm², FF= 56.3%, η = 11.1%) with respect to the reference P3HT-based PSC (η = 4%) and show a growing trend with respect to the fresh devices. The higher η is associated with the increase of the photo-generated current (J_{sc}), being the other device figure of merit, *i.e.*, open circuit voltage (V_{oc}) and fill factor (FF), remaining almost unchanged with respect to the ones of the reference PSC. The devices we fabricated with the GNP-PhOMe/P3HT blends have, instead, a different trend with respect to the one reported for the SWCNTs-based PSCs. Although the GNP-based PSCs all have a higher η (~8-9%) with respect to the reference PSC (η ~6.5%), only the device with 4% GNP-PhOMe/P3HT blend as HTL maintains constant its η during the endurance test, while the others reported a drastic reduction in η just after encapsulation (15 h) and even more pronounced after 75 h.

Hole-mobilities of the functionalized CNS/P3HT blends compared to P3HT only thin films were not found to correlate with the increased efficiency and stability of the devices. Further investigations are currently ongoing with the aim of determining the basic working mechanisms leading to the enhanced performances recorded for the devices containing functionalized CNS/P3HT blends as HTLs.

References

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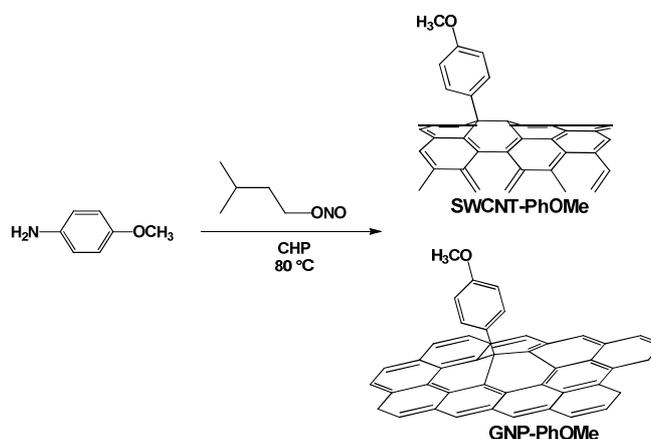


Figure 1. Functionalization of SWCNTs and GNPs via addition of the diazonium salt of 4-methoxyaniline.

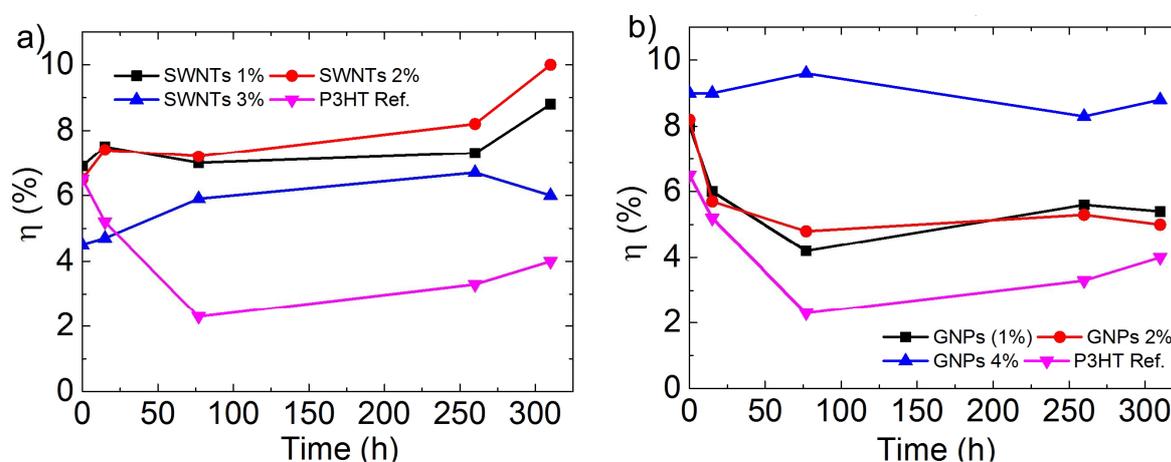


Figure 2. Endurance test for a) devices based on 1%, 2%, 3% SWNT-PhOMe/P3HT blends and b) 1%, 2%, 4% GNP-PhOMe/P3HT blends as HTL. In both graphs, the trend efficiency of the same device based on an undoped P3HT HTL is reported. After 15 h, all devices were encapsulated.