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Improved external quantum efficiency of solution-processed P3HT:60PCBM photodetectors by the addition of Cu–In–Se nanocrystals

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ABSTRACT

Photodetectors comprising a hybrid organic–inorganic photoconversion layer are prepared from solution under ambient conditions. Adding Cu–In–Se nanocrystals to a P3HT/60PCBM bulk heterojunction leads to a significant improvement of the maximum external quantum efficiency from 48% to 70% (at wavelength 520 nm) without impacting the temporal response or the linearity of the photodetector devices. This gain in efficiency with the addition of nanocrystals is attributed to the better light harvesting properties of the hybrid devices.

1. Introduction

Organic–inorganic hybrid materials consisting of conjugated polymers and semiconductor nanocrystals have been extensively studied for the photovoltaic conversion [1]. Inspired from organic photovoltaics, in hybrid materials the electron acceptor (nanocrystal) is dispersed in the electron donor phase (conjugated polymer) forming an interpenetrating network, the so-called bulk heterojunction. By using semiconductor nanocrystals instead of (6,6)-phenyl-C60-butyric acid methyl ester (60PCBM) as the electron acceptor the advantageous features of both the organic and inorganic compounds can be combined in a synergistic way. The optical and electronic properties of nanocrystals can be precisely tuned by changing their size (via the quantum confinement effect) and composition. Moreover, many inorganic semiconductors show high absorption coefficients and materials can be found to absorb light in the infrared range, difficult to attain with organic semiconductors. Conjugated polymers, on the other hand, exhibit good charge carrier transport and film-forming properties and also contribute to the light absorption in the visible range. Finally, the possibility to use solution based processes for depositing hybrid materials allows fabricating low cost optoelectronic devices. Nevertheless it is not trivial to optimize the composition and morphology of the hybrid heterostructures, which depend on numerous parameters. Efficient charge transport through the nanocrystal phase requires the formation of a percolating network. The latter can more easily be achieved with 60PCBM due to its smaller dimensions and similar chemical nature with the polymer matrix. By consequence, more recently the use of ternary blends comprising both nanocrystals and 60PCBM in combination with conjugated polymers has been explored [2,3].

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In the case of "plastic" photodetectors, the use of hybrid materials could in principle be even more interesting than in the case of solar cells. The main parameters characterizing a photodetector are the detectivity, response time and spectral range of detection, while not necessarily a high output power has to be achieved as in the case of solar cells. Both binary (polymer:nanocrystal) and ternary (polymer:60PCBM:nanocrystal) hybrid materials have been investigated [4–7]. Rauch et al. demonstrated in their seminal work that bulk heterojunction photodetectors containing PbS nanocrystals in combination with poly (3-hexylthiophene) (P3HT) and 60PCBM can detect near-infrared light up to 1.8 μm with an external quantum efficiency (EQE) up to 51% [4]. Here we investigate the use of copper indium selenide (Cu–In–Se) nanocrystals in hybrid photodetectors. Among their attractive features they offer a high absorption coefficient ($\alpha \sim 10^5\ cm^{-1}$), good chemical stability and high power conversion efficiency in solar cells [8–12]. The use of Cu–In–Se nanocrystals in optoelectronic devices is also motivated by the need to avoid materials containing toxic elements such as Cd, Pb or Hg, which are hazardous for human health and environment. So far Wang et al. [6] and Yang et al. [7] applied $CuInSe_2$ nanocrystals in combination with P3HT in binary blends and studied their photodetection behavior. In the former case, *I*/*V* measurements have been performed on a device obtained by drop-casting a P3HT:$CuInSe_2$ nanocrystals mixture (1:2 weight ratio) on a Si/SiO_2 substrate containing Pt electrodes. The current under illumination was around two orders of magnitude higher than the dark current and a power dependence of 1.34 was observed between the current and the incident light intensity [5]. In the latter case, different polymer:nanocrystal weight ratios were investigated, and the active layer was sandwiched between non-symmetrical electrodes (ITO/Al). For a 19:1 P3HT: nanocrystal ratio, photoconductivity was observed with a photocurrent-to-dark current ratio of 700 at a bias of −4 V. In both examples no measurements of the external quantum efficiency (EQE) have been reported. In this work, we study the photodetection behavior of ternary blends consisting of as-synthesized or surface ligand exchanged Cu–In–Se nanocrystals, regioregular P3HT and 60PCBM. Ligand exchange with shorter molecules is generally carried out in order to enhance the charge carrier transfer and transport in hybrid materials [13–16]. However, as we demonstrate here the use of as-synthesized, dodecanethiol-capped Cu–In–Se nanocrystals results in a considerable increase of the photodetection performance when compared to blends containing nanocrystals ligand exchanged with 2-ethylhexanethiol, i.e. a ligand of around half the length of the initial one. The hybrid device also outperforms the fully organic P3HT:60PCBM device pushing the maximum EQE from around 50% to 70% at wavelength 520 nm, at −2 V bias.

2. Experimental

The Cu–In–Se nanocrystals for the fabrication of photodetectors were synthesized using the general protocol for transferring metal ions from water to organic medium reported by Yang et al. [17]. In the first step, 0.25 mmol of $CuSO_4{\cdot}5H_2O$ and 0.25 mmol of $InCl_3$ were dissolved in 5 mL of deionised water each. Then 10 mL of ethanolic solutions of oleylamine (OLA, 6 mL in 45 mL of ethanol) were added to each metal ion solution. The extraction of the metal ions to the organic phase was performed by adding 6 mL of toluene and vigorous shaking in a separation funnel. Next, the aqueous phases were discarded and 10 mL of OLA was added to the combined toluene phases in a 3-neck 50 mL flask. The mixture was degassed at 60 °C for 60 min and then heated under argon to 130 °C for 10 min. After increasing the temperature to 160 °C the selenium reactant, prepared by dissolving 0.158 g of Se powder in 2.5 mL of trioctylphosphine (TOP), was injected. Immediately after the injection of the Se reactant, the temperature of the reaction mixture was increased to 240 °C. After 1 h the solution was cooled down to room temperature and the nanocrystals were isolated by addition of ethanol and centrifugation at 8000 rpm for 3 min. They were then dispersed in 1,2-dichlorobenzene and centrifuged at 7000 rpm for 5 min to remove aggregated particles. Using EDX spectroscopy and powder X-ray diffraction, we determined that cubic $Cu_{0.8}In_{1.2}Se_2$ nanocrystals were obtained with a mean diameter of 15 nm. For the ligand exchange with 2-ethylhexanethiol, the NCs were introduced to the 2-ethylhexanthiol solution. The mixture was heated under permanent stirring in an oil bath for 20 h at 55 C. The effectiveness of ligand exchange procedure was investigated by means of nuclear magnetic resonance (not presented here). Photodetectors were prepared under ambient conditions and their layered structure can be written as ITO/PEDOT:PSS/P3HT:60PCBM:Cu–In–Se(1:1:*x*)/Al with $x = 0$; 0.5 or 1. Commercial regioregular P3HT (SP001 from Merck) and 60PCBM from Nano-C were used. In the following, 1:1 denotes the reference blend without nanocrystals, produced from a 1,2-dichlorobenzene solution containing P3HT and 60PCBM in concentrations 60 mg/mL. Similarly, 1:1:0.5 and 1:1:1 denote the ternary blends resulting from addition of the nanoparticles to the reference blend, in the given weight ratio of the compounds. The blends with nanoparticle concentration exceeding 1:1:1 exhibited pronounced phase separation and they have not been further studied.

All devices were fabricated the same way. The 250 ± 10 nm thick active layer was spin-coated on a pre-patterned ITO/PEDOT:PSS substrate at low spin speed (800 rpm) during 180 s. The solvent and the spin speed were chosen because of the reported favorable self-organization of the materials in the layer [18]. The top aluminum electrode was evaporated under vacuum. The photodetectors were encapsulated with thin glass sheet pasted with epoxy glue purchased from DELO Company. Finally, the devices were annealed at 130 °C during 15 min.

Film thickness measurements were performed using a stylus profilometer (Ambios Technology XP-2). For film cross-section imaging, samples were broken in liquid nitrogen after spin-coating. Cross section images were taken using a Zeiss Ultra-55 scanning electron microscope.

X-ray diffraction measurements were carried out in the Bragg–Brentano reflection geometry using a Panalytical Empyrean diffractometer provided with a cobalt radiation

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