

Hybrid polymer solar cells based on zinc oxide

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We describe a new method towards low-cost, environmentally friendly solar cells. In a simple straightforward procedure, bulk heterojunction hybrid polymer solar cells are made by blending ZnO nanoparticles and a conjugated polymer into a thin film. The efficiency of this new type of solar cell represents a fourfold improvement compared to existing hybrid solar cells based on metal oxides and is similar to those based on cadmium selenides.

Hybrid polymer solar cells use a combination of a conjugated polymer and an inorganic semiconductor to convert sunlight into charges. The use of two

materials with complementary p and n type electronic properties is crucial to the operation of any (hybrid) polymer solar cell because photoexcitation of a conjugated polymer provides a bound electron-hole pair or exciton rather than free charges.^{1,2} This exciton can be dissociated efficiently at the interface with a second material *via* a hole or electron transfer to produce the free

charges that generate the photovoltaic effect. A complication arises because the exciton in conjugated polymers has a short lifetime (often sub-nanosecond) and a correspondingly small (5–10 nm) diffusion range. To ensure quantitative charge carrier generation, many organic and polymer solar cells are therefore designed to have a large area interface at short (nanometre) distances from anywhere within two materials by either using a nanoporous structure,³ or *via* a bulk heterojunction in which the two materials are mixed on a nanometre scale.^{4,5} A second prerequisite for an efficient photovoltaic device is that both the p and n type material have continuous percolation pathways to transport the photogenerated holes and electrons to the electrodes. Although intimate mixing and co-continuous percolation may seem difficult to realize simultaneously, various efficient bulk heterojunction photovoltaic devices have been reported in recent years using

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polymer composites,⁴ polymer–fullerene blends,^{6–8} or small molecule mixtures.^{9–12}

Compared to these cells, hybrid polymer solar cells may have the advantage of being morphologically more stable and being able to utilize the high charge carrier mobility of the inorganic material. Of course the challenge for hybrid polymer solar cells remains to create a morphology in which the inorganic and polymeric materials are intimately mixed on a nanometre scale but with co-continuous phases. This is well illustrated by the work of Alivisatos *et al.* on CdSe nanoparticles mixed with regioregular poly(3-hexylthiophene) (P3HT).^{13,14} By modifying the surfactant shell of CdSe it was possible to create sufficient dispersion of the nanoparticles in a solvent for processing and to enable charge transport between individual particles in the resulting hybrid polymer film. Hybrid bulk heterojunction polymer solar cells with power conversion efficiency (η) of 1.7% under simulated solar light (AM1.5) and monochromatic external quantum efficiency (*EQE*) of 55% were made from CdSe nanorods.¹³ Recently, higher values ($\eta = 2.4\%$ and *EQE* = 52%) were achieved by Greenham *et al.* who introduced branched nanorods and stratification of layers in a successful attempt to improve charge transport.^{15,16} These hybrid solar cells are currently the best performing hybrid photovoltaic devices, but their elaborate, high-temperature synthesis and the undesirable use of toxic CdSe motivate the search for alternative materials.

Transparent semiconducting metal oxides like TiO₂ and ZnO can also be used as the electron accepting material in combination with *p*-type conjugated polymers. These metal oxides are not considered to be toxic and are available in abundance. Inspired by the dye-sensitized solar cells that provide efficiencies up to $\eta = 10\%$,¹⁷ many studies have been directed to filling a nanoporous TiO₂ phase with a conjugated polymer. Several reports explain how filling of nanoporous TiO₂ with conjugated polymers can be accomplished, resulting in nanoporous TiO₂ : polymer solar cells.^{18–21} McGehee *et al.* prepared nanostructured TiO₂ films that have a regular and open structure with pores of approximately 10 nm using the structure directing properties of block copolymers.

The pores were filled when a film of regioregular P3HT, deposited on top of this porous TiO₂, was heated above its melting temperature.¹⁸ Solar cells based on such infiltrated TiO₂ : P3HT layer and a 30 nm P3HT overlayer gave a maximum *EQE* = 10% and an estimated $\eta = 0.45\%$ under AM1.5 conditions.¹⁹ We note, however, that very recent evidence suggests that filling of nanoporous TiO₂ by P3HT cannot always be accomplished.²² In a related approach, Nelson *et al.* showed that penetration of conjugated co-polymers into thin porous TiO₂ films can be achieved by dip coating the substrate into a solution of the polymer in an organic solvent.²⁰ Using a cell configuration in which the mixed TiO₂ : polymer layer was sandwiched between dense TiO₂ and pure polymer layers, cells with $\eta = 0.41\%$ were obtained.²¹

The alternative approach, *i.e.* making bulk heterojunction solar cells by blending TiO₂ nanoparticles with conjugated polymers, is not straightforward. Early examples show only rather poor photovoltaic effects.²³ The synthesis of TiO₂ nanoparticle powders mainly occurs in water or alcohol based media. Transferring these nanoparticle powders into organic solvents regularly leads to aggregate formation and therefore a low miscibility with conjugated polymers. For this reason the application of TiO₂ nanoparticle powders in the bulk heterojunction approach is often limited. Only recently it was shown that TiO₂ nanopowders and conjugated polymers can be blended from common organic solvents. Kwong *et al.*²⁴ demonstrated solar cells with an efficiency of approximately $\eta = 0.42\%$, providing a first account showing that the ideas advanced by Alivisatos for CdSe, also work for TiO₂ nanoparticles.

In our first approach to make hybrid bulk heterojunction polymer solar cells, we aimed to circumvent both the filling problem and the mixing problem. A precursor for TiO₂, Ti(i-PrO)₄, was added to a solution containing MDMO-PPV (Fig. 1a) prior to spin casting a film. This Ti(i-PrO)₄ precursor was converted *in situ* into TiO₂²⁵ by exposure of the cast film to moisture and a consecutive high vacuum treatment. Photovoltaic devices prepared using this simple approach gave efficiencies up to $\eta = 0.2\%$ and *EQE* = 11%.^{25,26} The main drawback of

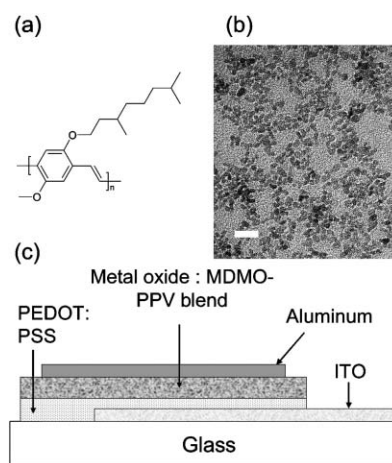


Fig. 1 Materials and device layout. (a) Structure of MDMO-PPV. (b) TEM photograph of ZnO nanoparticles, bar indicates 20 nm. (c) Device structure consisting of a ~100 nm thick hybrid polymer blend, sandwiched between ITO/PEDOT : PSS and aluminium electrodes on a glass substrate.

the use of TiO₂ is that crystallization requires high temperatures (>350 °C²⁷) and hence we assume that the presence of an amorphous, rather than a crystalline, network of TiO₂ limits the charge transport in these photovoltaic devices.

Our new approach seems to circumvent many of the drawbacks associated with previous methods and uses ZnO instead of TiO₂ or CdSe. We were able to make soluble crystalline ZnO nanoparticles (*nc*-ZnO) that can easily be blended with conjugated polymers without the use of surfactants.²⁸ Fig. 1b shows a transmission electron microscopy image of crystalline ZnO nanoparticles of approximately 4.9 nm in diameter (according to UV absorption onset). Spin casting a mixed solution of *nc*-ZnO particles and a conjugated polymer (MDMO-PPV) from a common solvent (chlorobenzene–methanol 95 : 5 v/v) was used to prepare thin bulk heterojunction films. Transmission electron microscopy (TEM) of a thin (50 nm) film (Fig. 2a) containing 26 vol% ZnO revealed phase separation on nanometre scale; dark *nc*-ZnO regions and bright polymer regions, some bigger than 10 nm, can be seen. Atomic force microscopy (AFM) of a thicker (100 nm) layer (Fig. 2b) reveals sphere like structures at the surface and a film roughness of 4 nm (rms).²⁹

Photoinduced absorption spectroscopy (PIA) gives direct spectral evidence

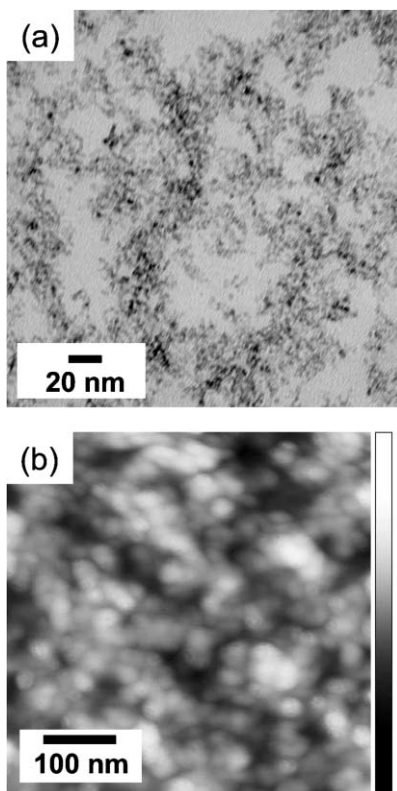


Fig. 2 (a) TEM photograph and (b) tapping mode-AFM height image of a thin *nc*-ZnO : MDMO-PPV films (AFM height scale = 50 nm). For more details see ref. 29.

that under illumination electron transfer occurs from the polymer to the ZnO nanoparticles. The PIA spectrum (Fig. 3a, solid line) of the *nc*-ZnO : MDMO-PPV blend exhibits the characteristic absorption bands of the polymer radical cation at 0.4 and 1.3 eV.³⁰ Compared to the spectrum of TiO₂ : MDMO-PPV (Fig. 3a, dashed line), the increased intensity of the 0.4 eV band indicates the presence of negatively charged *nc*-ZnO.³¹ Pump-probe spectroscopy (Fig. 3b) revealed that the photo-induced charge transfer occurs within a picosecond, similar to the ultrafast electron injection (<300 fs) reported by Bauer *et al.*³² for Ru(dcbpy)₂(NSC)₂ dyes on nanoparticle ZnO electrodes.

Hybrid *nc*-ZnO : MDMO-PPV bulk heterojunction photovoltaic devices (Fig. 1c) were made by spin casting a mixed solution of *nc*-ZnO particles and a conjugated polymer (MDMO-PPV) onto a film of poly(3,4-ethylenedioxythiophene) : poly(styrenesulfonate) (PEDOT : PSS, Bayer AG) that was deposited on a UV-ozone cleaned indium

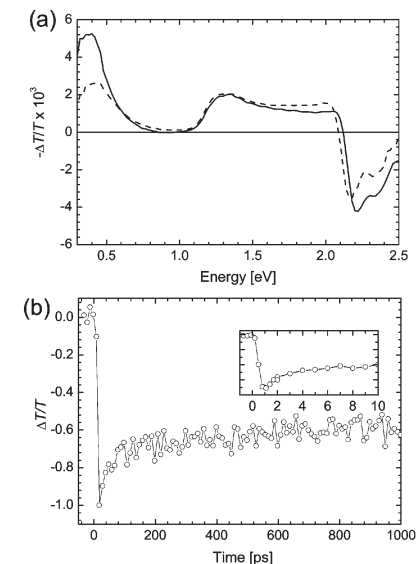


Fig. 3 (a) Near-steady state photo-induced absorption (PIA) spectrum of a *nc*-ZnO : MDMO-PPV blend (solid line) and a *precursor*-TiO₂ : MDMO-PPV blend (dashed line) measured at 80 K with excitation at 488 nm. (b) Time-resolved pump-probe spectroscopy of a *nc*-ZnO : MDMO-PPV blend measured at room temperature, monitoring the intensity of the radical cation band at 0.56 eV (2200 nm), after excitation at 2.43 eV (510 nm) with 200 fs pulses. The inset shows the transient absorption at short time delays.

tin oxide (ITO) coated glass substrate. The back electrode, consisting of 100 nm Al, was evaporated in a high vacuum. The *EQE* of the hybrid *nc*-ZnO : MDMO-PPV solar cell with 26 vol% ZnO (Fig. 4a) has been measured with white light bias illumination to create conditions resembling operation under solar illumination. The *EQE* spectrum reaches a value of 40% at the absorption maximum of MDMO-PPV. Integration of the *EQE* with the solar spectrum (AM1.5 standard, normalized to 100 mW cm⁻²) affords an estimate of the short-circuit current density of $J_{SC} = 3.3 \text{ mA cm}^{-2}$ under AM1.5 (1 sun) conditions. *J-V* measurements measured with white-light illumination (equivalent to AM1.5 at 71 mW cm⁻²)²⁸ are shown in Fig. 3b. Under these conditions $J_{SC} = 2.40 \text{ mA cm}^{-2}$ has been obtained, together with an open-circuit voltage (V_{OC}) 814 mV and a fill factor (*FF*) of 0.59 (Fig. 4b). At this light intensity the power conversion efficiency is $\eta = 1.6\%$. Solar cells have also been made with smaller ZnO nanoparticles (3.7 nm

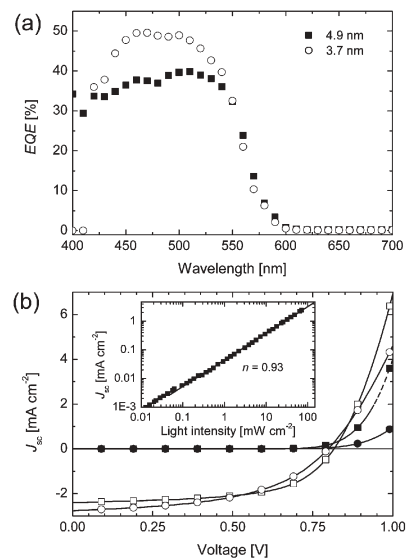


Fig. 4 Photovoltaic device characterization of *nc*-ZnO : MDMO-PPV (26 vol% *nc*-ZnO) solar cells with 4.9 and 3.7 nm ZnO nanoparticles. (a) *EQE* as function of the wavelength of monochromatic irradiation for 4.9 nm (solid squares) and 3.7 nm (open circles) particles; (b) *J-V* characteristics in the dark (solid symbols) and under illumination with white light from a tungsten halogen lamp estimated at 0.71 sun equivalent intensity (open symbols) for 4.9 nm (squares) and 3.7 nm (circles) particles.

instead of 4.9 nm according to UV).²⁹ The smaller nanoparticles gave photovoltaic devices with an increased *EQE* = 50%, but slightly lower $V_{OC} = 800 \text{ mV}$ and $FF = 0.50$ (at 71 mW cm⁻²) (Fig. 4). Integrating the *EQE* gives an estimated $J_{SC} = 3.9 \text{ mA cm}^{-2}$ at AM1.5 (100 mW cm⁻²) and $\eta = 1.6\%$, similar to that for the device based on the 4.9 nm sized particles.

Light intensity dependent *J-V* measurements for the *nc*-ZnO : MDMO-PPV cells show a slightly sub-linear increase of J_{SC} with light intensity (*I*): $J_{SC} \propto I^n$, with $n = 0.93$ (inset of Fig. 4b). This near-linear relation implies that only minor bimolecular charge carrier recombination occurs in these photovoltaic devices under short circuit conditions.

It is of interest to compare the performance of these cells with other hybrid cells. Polymer-metal oxide solar cells using nanoporous or nanoparticle TiO₂ and a conjugated polymer reach power conversion efficiencies of $\eta = 0.40\text{--}0.45\%$.^{19,21,24} Hence, with $\eta = 1.6\%$ the *nc*-ZnO : MDMO-PPV solar cell

represents a fourfold improvement. However, the performance is less than that of the best CdSe : polymer cells. Cells based on CdSe tetrapods and MDMO-PPV in a stratified layer reach $J_{SC} = 6.42 \text{ mA cm}^{-2}$, $V_{OC} = 760 \text{ mV}$, $FF = 0.44$ (at 89.9 mW cm^{-2} AM1.5) and $EQE = 52\%$, leading to $\eta = 2.4\%$.¹⁶ Compared to this device, the *nc*-ZnO : MDMO-PPV cells have a higher V_{OC} and FF , but a lower J_{SC} . The lower J_{SC} is mainly attributed to the fact that, in contrast to CdSe, ZnO does not absorb light in the visible region. As a result, the inorganic phase contributes to the current in the CdSe cells by hole transfer in the visible region, even up to 675 nm, which is beyond the absorption region of the polymer. Nevertheless, the efficiency of the ZnO based devices is still remarkable. Despite the reduced absorption, the maximum EQE under short circuit conditions is very similar (50% for ZnO and 52% for CdSe) within the absorption band of the polymer. This suggests that charge generation and transport by ZnO nanoparticles is similar, or could even be superior, to that of extended CdSe structures.

In conclusion, the easy synthesis of ZnO nanoparticles without the need to use additional surface modification to create solubility in organic solvents represents a major advantage compared to existing methods based on TiO₂ or CdSe. The external quantum efficiencies and power conversion efficiency of the novel *nc*-ZnO/MDMO-PPV devices represent a significant improvement compared to existing hybrid polymer solar cells using TiO₂ and are similar to CdSe : polymer cells. In our view this demonstrates the use of ZnO nanoparticles as a

promising material for application in hybrid polymer solar cells.

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