A Nanocomposite Ultraviolet Photodetector based on Interfacial Trap-Controlled Charge Injection

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Materials

2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) (HOMO: 6.4 eV, LUMO: 2.9 eV)¹ and polyvinylcarbazole (PVK) were purchased from SIGMA-ALDRICH; poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) (PH4083) was purchased from
H.C.STARCK; poly-3(hexylthiophene)(P3HT) was purchased from Rieke Metals (HOMO: 5.1 eV LUMO: 3.2 eV)\(^2\). All materials were used as received without any purification. 4,4’-Bis[(p-trichlorosilylpropyl phenyl)phenylamino]-biphenyl (TPD-Si\(_2\)) was synthesized following the route from literature \(^3\). (PVK:TPD blend layer HOMO: 5.5 eV, LUMO:2.4 eV)\(^4\) Fig. S1 shows the chemical structures of the materials used in our devices.

Fig. S1 Chemical structures of the materials

**Methods**

**Synthesis of ZnO Nanoparticles**

ZnO nanoparticles were prepared by hydrolysis method in methanol with some modifications\(^5,6\). In brief, 2.95 g (23 mmol) ZnAc\(_2\)·2H\(_2\)O was dissolved in 125 ml MeOH at 60 °C and followed by adding KOH solution (1.57g KOH in 65 ml MeOH) within 5 minutes. After around 1.5 hour, when the reaction solution became turbid from transparent, the reaction mixture was stirred for one more hour. The small size nanoparticles were collected by centrifuge and were washed by methanol for three times, and then dispersed in chlorobenzene to form transparent solution. The average size of the ZnO nanoparticles made by this method is around 5 nm (VB= 7.65 eV   CB= 4.3 eV)\(^7\).
**Device Fabrication**

For the device fabrication, PEDOT: PSS was first spin-coated onto a cleaned ITO glass substrate at a spin speed of 3,000 r.p.m., which gives a PEDOT: PSS film thickness of approximately 30 nm. The PEDOT:PSS was then baked at 120 °C for 30 minutes before spin-casting the polymer film. Poly vinylcarbazole (PVK) was first dissolved in 1,2-dichlorobenzene (DCB) to make 20 mg/ml solution, followed by blending with 4,4′-Bis[(p-trichlorosilylpropylphenyl)phenylamino]-biphenyl (TPD-Si₂) with a ratio of 1:1 by weight. TPD-Si₂ was a cross-linkable, hole-transporting organosiloxane material. The hole-transporting layer was obtained by spin-coating the blend at 4000 r.p.m. for 20 s, and the thickness of the blend film is approximately 70 nm. The film was then annealed at 100 °C for 1 hour in air to crosslink TPD-Si₂. The photoactive layers were made of blends of ZnO nanoparticles with PVK or P3HT at the ratio of 3:1 by weight. The solutions were spin-coated at 1000 r.p.m. for 25 s, then solvent annealed for eight hours by placing the devices in the vapor of the solvent which significantly slows down the drying of the polymers. P3HT can form crystalline phase by the solvent-annealing which increases the hole mobility of the photoactive layer. The thicknesses of the active layers were around 500 nm. A BCP layer of around 10 nm was deposited by thermal evaporation onto the photoactive layer. To finish the device fabrication, a 100 nm thick aluminum was thermally evaporated on the photoactive layer as the cathode. The active device area is 0.05 cm² which is defined by the shadow masks.

**Verification of electron trapping in active layer**

In order to verify the electron trapping in the nanocomposite layer, hole-only and electron-only devices have been made. The electron only devices and hole only devices have structures of ITO/Cs₂CO₃/P3HT:ZnO/Cs₂CO₃/Al and ITO/PEDOT:PSS/P3HT:ZnO/MnO₃/Al, respectively. The 1-3 nm thick Cs₂CO₃ layers formed by spin-coating or thermal evaporation result in a low work function surface so that only electrons can be injected. Similarly high work function interlayers such as PEDOT:PSS and MnO₃ guarantee hole injection only.

The current density in hole-only device is 3-4 orders of magnitude higher than electron-only device. This indicates that electrons can hardly move in the active layer due to the trapping of
them by ZnO nanoparticles. On the other hand, holes can freely move with a relatively high mobility and thus enables the high photoconductive gain in our devices. Fig. S2 are J-V curve fitting for the electron-only and hole-only devices with the space charge limited current, respectively. The derived mobilities are $1.9 \times 10^{-3}$ cm$^2$/V·s for holes and $2.0 \times 10^{-6}$ cm$^2$/V·s for electrons in P3HT:ZnO film.

Fig. S2 J-V curve fitting of electron-only and hole-only devices of (a) P3HT:ZnO device and (b) PVK:ZnO

Nanocomposite film characterization

The Electrostatic force microscopy (EFM) was used to characterize the topography and electron trap distribution in the nanocomposite films. EFM maps electric properties on a sample surface by measuring the electrostatic force between the surface and a biased AFM cantilever. EFM applies a voltage (+1 V in our measurement) between the tip and the sample, while the cantilever hovers above the surface not touching it. The cantilever deflects when it scans over static charges. The force arises from Coulomb interactions of the stored charge in ZnO nanoparticles, its image charges in the tip, and the induced charges due to the voltage EFM applied during imaging. The topography image shows a peak-valley difference of 20 nm which should be the size of ZnO NP aggregations. The nanocomposite surface was found to be covered by a high density of ZnO nanoparticles with a high coverage. The electrostatic force image agrees with the topography
image very well. Larger electrostatic force between the ZnO nanoparticles and the tip (+1 V) was clearly observed which confirms the electron traps by the ZnO nanoparticles.

Fig. S3 EFM topography (a) and the electrostatic force image (b) of the nanocomposite film
Scan size: 2 µm × 2 µm

The cross-section morphology of the P3HT:ZnO nanoparticles nanocomposite was also measured by scanning electron microscopy (SEM). SEM was performed on a Quanta 200 FEG SEM at high vacuum mode. The sample was prepared by cutting the P3HT:ZnO nanoparticles nanocomposite films on ITO glass after soaking them in liquid nitrogen in order to obtain a sharp cross-section. Figure S4 shows the cross-section SEM of the nanocomposite film. A vertical composition profile is clearly observed: ZnO nanoparticles (bright color) prefer to stay close to the top surface while P3HT (dark color) is distributed close to the ITO substrate side. This agrees with the EFM measurement which shows the surface of the nanocomposite film is predominately occupied by ZnO nanoparticles.
Device characterization

The external quantum efficiency was measured with the Newport QE measurement kit by focusing monochromatic beam of light onto the devices. The incident light was chopped at 35 Hz, and the optical power density is controlled to be around 1 μW/cm². A Si diode which has calibrated response from 280 nm to 1100 nm was used to calibrate the light intensity for photocurrent measurement.
For the transient response measurement, an optical chopper was used to get the light pulse of 800 Hz; a small resistor of 100 Ω was connected in series with the photodetector and a high speed and sensitive oscilloscope (LeCroy WaveRunner 104Mxi-A, 1 GHz, 10 GS/s) was used to record the voltage variation of the resistor. The resistance of the device is above 45 kΩ under light. The small resistor used won’t perturb the circuit because it is much smaller than the resistance of the device. The absorption spectra of the photo active layers of PVK:ZnO and P3HT:ZnO were measured with PerkinElmer Lambda 900 spectrometer. The film thickness was measured with AMBIOS XP-2 stylus profilometer. All the measurements were carried out at room temperature in the ambient condition.

EQE was measured for 10 cycles at -9 V to check the device stability. As shown in Fig.S5, the EQE at 360 nm are almost constant during this measurement.

![Fig. S5 Measured EQE at reverse bias of -9 V repeated for 10 circles.](image)

**Dynamic range measurement**

For light intensity below 1 μW/cm², the monochromatic illumination was provided by a 350 nm LED with a PROTEK B8020FD function generator to supply a modulated bias to the LED. For higher light intensity up to 0.1 W/cm², the light was provided by Xe lamp. The UV part of the light from Xe lamp is calculated by the integration of UV light intensity from Xe lamp spectrum. The photocurrents at different light intensities were recorded with a Lock-In Amplifier SR830 at a fixed frequency of 35 Hz.
In both cases, the irradiance was calibrated with a Si diode at highest light intensity of each light source and Newport neutral density filters were used to modulate the light intensity from 0.1 W/cm² to 1 pW/cm².

**Calculation of hole mobility and photoconductive gain**

For the case of trap-free or a discrete set of shallow traps space-charge limited current, the dependence of current and voltage obeys Child’s law\(^{11}\):

\[
J = \frac{9}{8} \varepsilon_r \varepsilon_0 \mu \frac{V^2}{d^3}
\]  

(1)

where \(\varepsilon_r\) is the relative dielectric constant, \(\varepsilon_0\) is the permittivity of vacuum, \(\mu\) is the effective charge carrier mobility, \(d\) is the organic layer thickness and \(V\) is the applied voltage.

Using \(\varepsilon_r = 3\) for PVK and P3HT\(^{12,13}\), \(d = 500\) nm, \(V = 9\) V, thus the hole mobility in the PVK : ZnO and P3HT : ZnO blend films can be determined using equation (1). The simulated hole mobility is \(9.8 \times 10^{-4}\) cm²/V·s and \(1.9 \times 10^{-3}\) cm²/V·s for PVK : ZnO and P3HT : ZnO, respectively. The magnitude of these mobilities agrees well with many other reported\(^{14-17}\).

Assuming the detector works in the pure photoconductor region, the photoconductor gain \((G)\) can be calculated by the ratio of the recombination lifetime \((\tau_{\text{life time}})\) and transit time \((\tau_{\text{transit}})\) of the holes:

\[
\begin{align*}
G &= \frac{\tau_{\text{life time}}}{\tau_{\text{transit}}} \\
\tau_{\text{transit}} &= \frac{d}{\mu_p E} \\
E &= \frac{V}{d}
\end{align*}
\]  

(2)

Where \(d\) is the inter electrode spacing, \(V\) is the applied bias, \(\mu_p\) is the hole mobility and \(E\) is the electric filed. Using the hole recombination lifetime of 558 \(\mu\)s from the transit photo response measurement, \(V = 9\) V, \(d = 500\) nm, \(\mu_p = 1.9 \times 10^{-3}\) cm²/V·s, the calculated photoconductor gain of P3HT : ZnO device is 3,798. It is very close to the measured gain by IPCE.

**Noise current measurement and detectivity calculation**
The noise current was directly measured with a Stanford Research SR830 Lock-In Amplifier as reported by Konstantatos, G. et al.\textsuperscript{18,19}. The devices were biased using alkaline batteries, and testing was carried out in an electrically shielded and optically sealed probe station, and on a floating table to minimize the vibrational noise. Through the choice of integration time, 1 s for our measurement, lock-in amplifier reported a noise current normalized to the measurement bandwidth in A/Hz\textsuperscript{1/2}.

The specific detectivities were calculated with the measured noise using the methods reported in reference\textsuperscript{18}. The NEP was calculated by dividing noise current with the responsivity under the same measurement frequency and bias. The specific detectivity D* was obtained as a function of wavelength, applied bias, and center frequency by dividing the square root of the optically active area of the device by the NEP.

\textbf{Supplementary References}


