

Simple near-infrared photodetector based on charge transfer complexes formed in molybdenum oxide doped N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine

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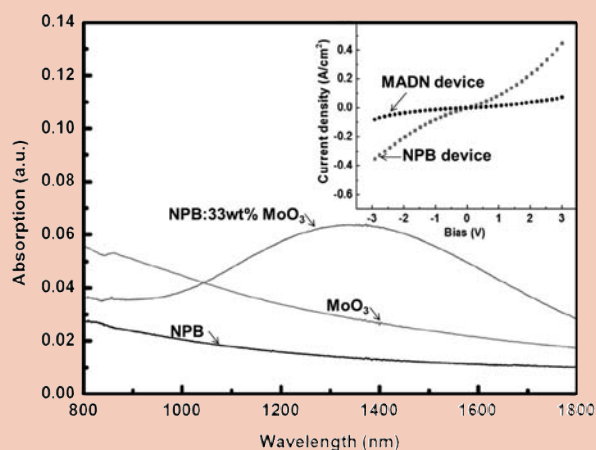
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We have demonstrated a simple near-infrared (NIR) photodetector (PD) based on charge transfer complex (CTC) formed in molybdenum trioxide (MoO_3) doped N,N'-di(naphthalene-1-yl)-N,N'-diphenyl-benzidine (NPB), which shows a photocurrent of about 0.35 A/cm^2 at -3 V under 980 nm illumination. The existence of CTC formation promotes photocurrent generation which is investigated by comparison with MoO_3 doped 2-methyl-9,10-di(2-naphthyl)anthracene (MADN) film which has no CTC absorption. It can be evolved that this kind of simple-structure photodetector has potential application in the near-infrared (NIR) detection area. It is shown in this Letter that although both MoO_3 and NPB have larger energy gaps of about 3 eV and weak absorption in the NIR region, the charge transfer complexes formed by mixing the two materials show an extra absorption band and good photoelectric response in the NIR region.



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In recent years, organic near-infrared (NIR) photodetectors (PDs) have been widely studied due to their tremendous potential in industrial and scientific applications, such as remote control, chemical/biological sensing, optical communication, and spectroscopic and medical instruments [1–6]. Yao and co-workers reported a near-infrared PD using low band gap polymer ester-functionalized polythieno[3,4-b]thiophene as donor (D) material and (6,6)-phenyl C61-butyric acid methyl ester (PCBM) as acceptor (A) [4]. More recently, Zimmerman and co-workers fabricated NIR PDs by spin-coating porphyrin tape as D

material [5]. So far, most reported organic NIR PDs are based on polymeric materials of low energy gap. As small molecular materials with low energy gap and good infrared response are rare, there are few reports on NIR PDs based on small molecular materials [7, 8]. In this work, we use an alternative approach to obtain NIR photoelectric responses by exploiting a charge transfer complex (CTC) formed between two large energy gap materials with no NIR photoelectric response.

A CTC is usually formed by transfer of an electron from the highest occupied molecular orbital (HOMO) of a

donor molecule to the lowest unoccupied molecular orbital (LUMO) of an acceptor molecule. CTCs have been studied for their potential applications in molecular magnets [9, 10], nonlinear optics [11], molecular electronics [12–14], and have been shown to enhance electrical conductivity [15], charge separation and transport etc. [16, 17]. Many groups have reported that metal oxides can form CTCs with organic materials by electron transfer from organic molecules to the oxides [18, 19]. It has also been observed that upon CTC formation, absorption spectra of the composite material would be considerably red shifted with respect to both of the constituting components [14]. However, so far this phenomenon has not been exploited in devices for making use of the red-shifted absorption spectra. We report a simple NIR PD using a blend of molybdenum trioxide (MoO_3) and N,N' -di(naphthalene-1-yl)- N,N' -diphenyl-benzidine (NPB) as the active layer. Based on a comparative study, we clearly demonstrate that the formation of CTC promotes charge generation and results in a photocurrent in the NIR range even though both MoO_3 and NPB have high energy gaps (both about 3.0 eV).

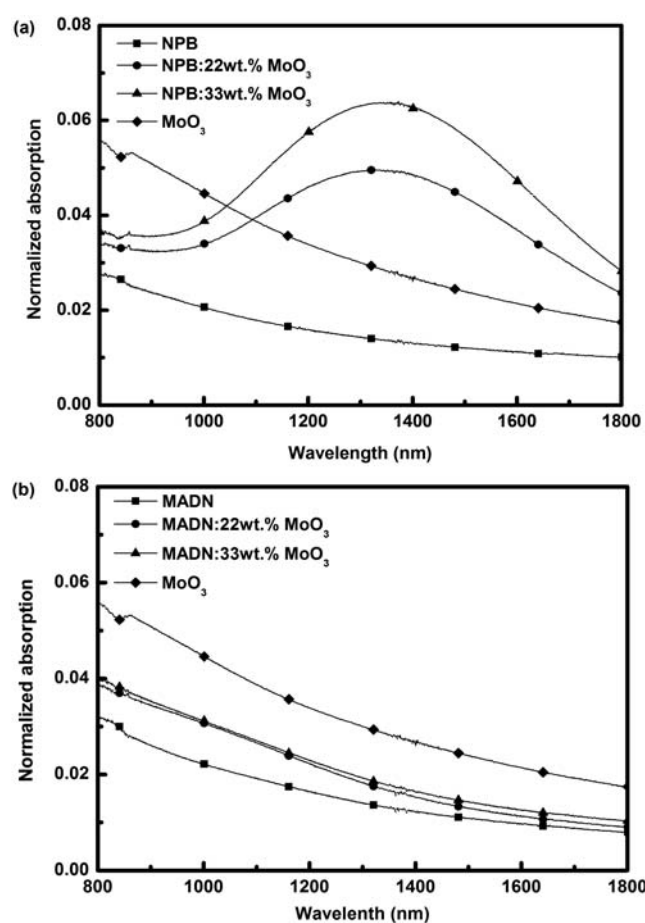


Figure 1 Normalized UV–Vis–NIR absorption spectra of NPB, MADN, MoO_3 , 22 wt% and 33 wt% MoO_3 doped NPB and MADN films, respectively.

All chemicals were purchased commercially and used without further purification. Organics and metal layers were sequentially deposited onto clean ITO glass substrates with a sheet resistance of $30 \Omega/\text{square}$ via shadow masks to form devices with an area of 0.1 cm^2 . ITO is treated for 20 min in an ultraviolet-ozone chamber before being put into the deposition chamber. Deposition rates and thicknesses of all layers were monitored *in situ* using an oscillating quartz monitor. All devices were encapsulated in a glove box immediately after fabrication. Absorption spectra of the organic films on quartz substrates were measured with a UV–Vis–NIR spectrophotometer (Lambda 750). Current–voltage (I – V) characteristics were measured with a semiconductor parameter analyzer (Keithly 4200-SCS) in dark and under illumination with a 980 nm laser.

Figure 1(a) shows normalized absorption spectra of 85 nm thick pristine films of NPB, MoO_3 , and MoO_3 :NPB blend films with different weight ratios on quartz substrates. The formation of CTC can be easily detected by the appearance of additional absorption peaks in the NIR region, which are not shown by either component. It can be clearly observed that there is a CTC absorption band around 1300 nm in the MoO_3 doped NPB films. Also the absorption intensity increases by increasing the doping ratio of MoO_3 , which is in consistency with the result reported by Shin et al. [20].

A device with the simple configuration of ITO/NPB: MoO_3 (33 wt%, 85 nm)/Al (150 nm) was fabricated. For comparison, a device with the configuration of ITO/2-methyl-9,10-di(2-naphthyl)anthracene (MADN): MoO_3 (33 wt%, 85 nm)/Al (150 nm) was also fabricated. Figure 2 shows the current–voltage characteristics for the two devices under 980 nm laser irradiation with a power of 1.3 W. The NPB-device shows a photocurrent of 0.35 A/cm^2 at -3 V . It is obvious that the photocurrent is

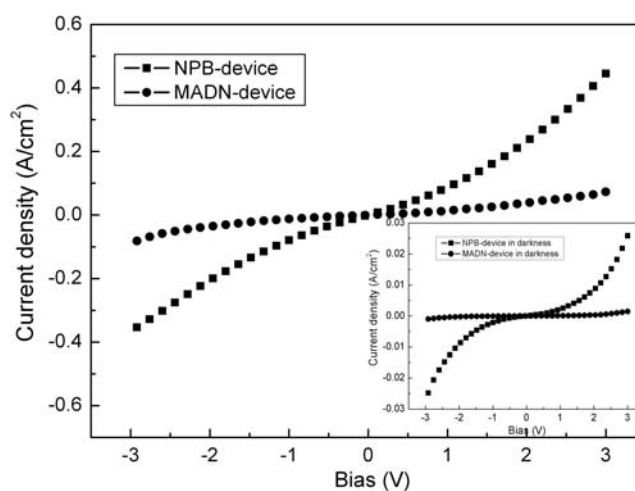


Figure 2 Current–voltage characteristics for the NPB-device and MADN-device under 980 nm laser irradiation with power of 1.3 W. Inset: Current–voltage characteristics in dark for the two devices.

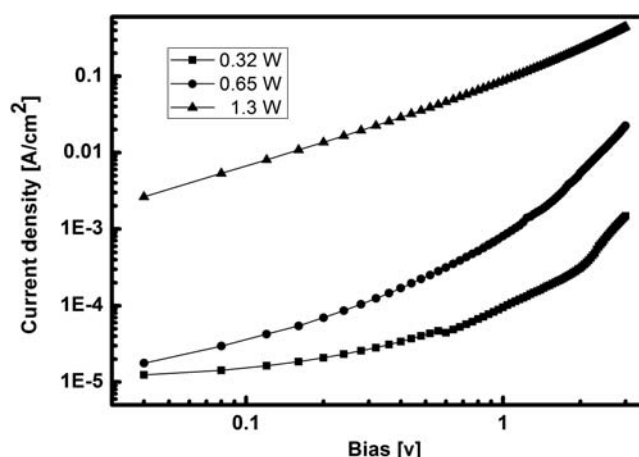


Figure 3 Current density of the NPB:MoO₃ device under different laser power.

larger for the NPB-device than for the MADN-device. The inset is the current–voltage characteristics in dark for the two devices. From the inset, we can see that the NPB-device also has a higher dark current, which may be due to the net charge carrier induced by CTC formation [21].

Figure 1(b) shows the normalized absorption spectra of 85 nm thick pristine films of MADN, MoO₃, and 22 wt% and 33 wt% MoO₃ doped MADN blend films. From Fig. 1(b), we can see that there is no CTC absorption in the MoO₃:MADN blend films, even though they have high absorption at 980 nm wavelength. This shows that the formation of CTC is in favor of photocurrent generation.

We also investigated the relationship between the photocurrent and the laser power, shown in Fig. 3. It is clear that the photocurrents increase with increasing laser power.

In conclusion, we demonstrated that the device with MoO₃ doped NPB as the active layer is promising for use in NIR photodetector applications. The existence of charge transfer complexes favors the photocurrent generation, comparatively proved by using a system without charge transfer complex formation based on the device with MoO₃ doped MADN as the active layer. The NIR detector has a photocurrent of 0.35 A/cm² at $\lambda = 980$ nm.

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