

Well-defined nanoarrays from an n-type organic perylene-diimide derivative for photoconductive devices

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Abstract

Well-defined one-dimensional (1D) perylene-diimide derivative (PDD) nanowire arrays were prepared via a simple electrophoretic deposition method by using anodic aluminum oxide (AAO) templates. The morphology of the as-deposited films was characterized by field emission scanning electron microscope and transmission electron microscopy. The highly ordered nanoarrays were free-standing after removing the AAO supports. Further studies revealed that the growth process of the nanowires in the AAO pores followed a 'bottom-up' growth model. A photoreceptor with PDD nanowire arrays as the charge generation layer was fabricated. It exhibited a better photoconductivity under light illumination when compared to that of its bulk counterpart. Our results suggested that electron-accepting PDD nanowire arrays can be used as a potential candidate for photoconduction devices, which would facilitate further exploration of new technological applications of the photoimaging process.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Fabrication of nanometer-scale components in desired geometries is of significance for the new generation of optoelectronic devices such as field-effect transistors, photovoltaic cells, light-emitting diodes, lasers, etc [1–4]. In particular, vertically aligned nanowire arrays with a high surface-to-volume ratio on conductive substrates are expected to have high charge carrier mobilities because of their well-defined transportation channels for carriers [5], and thus would be ideal building blocks for photovoltaic and photoconductive devices [6]. Many research groups have made great efforts to fabricate nanowires from a variety of materials including metals [7], metal oxides [8, 9] and polymers [10, 11], exploring a diversity of preparation techniques such as chemical vapor de-

position [12, 13], electrochemical deposition [14], template-wetting method, etc [15, 16].

Generally, two fundamental approaches for the preparation of nanowires have been investigated extensively: self-assembly of precursor compounds and template synthesis. The latter method, pioneered by Martin [17, 18], has proved to be a versatile approach for nanomaterial synthesis. Due to the convenience in controlling the size, especially the diameter of the as-prepared nanostructures, template synthesis has attracted much attention. Many research groups have used this method to prepare nanoscale materials by employing alumina membranes as templates [19, 20].

Perylene bisimides represent one of the most extensively studied classes of n-type organic semiconductors with potential applications in fluorescent solar collectors [21], photovoltaic devices [22], dye lasers [23] and molecular switches [24]. These dyes have not only outstanding chemical, thermal and

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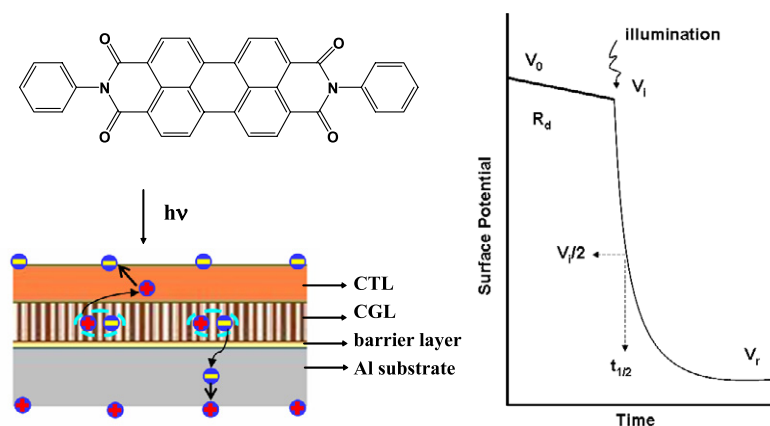


Figure 1. The molecular structure of PDD (top left), the schematic structure of the photoreceptor using PDD nanowire arrays as the charge generation layer (bottom left) and a typical photoinduced xerographic discharge curve (right), where V_0 is initial surface charge potential, R_d is dark decay, V_i is surface potential at illumination, $t_{1/2}$ is half-life time and V_r is residual surface charge potential.

photochemical stability, but strong absorption from the visible region to the NIR region and strong fluorescent emission with quantum yields near unity [25, 26]. So, constructing well-ordered and aligned perylene bisimide nanowires is of great interest both from a fundamental and a practical point of view. However, it is still a challenge to obtain highly ordered nanowire arrays by a facile and size-controllable fabrication technique.

Herein, we successfully fabricated the vertically oriented perylene-diimide derivative (referred to as PDD below) nanowire arrays against a conductive substrate via a simple electrophoretic template technique, a feasible and low-cost method for fabrication of organic nanowires [27–30]. A forest of free-standing and well-ordered PDD nanowire arrays was obtained after selectively removing the alumina templates. The diameter and the length of the PDD nanowires replicated the diameter of the pores and the thickness of the original template. The growth of PDD nanowires in the AAO pores follows the ‘bottom-up’ model, that is, the PDD molecules first deposited at the bottom of the AAO pores, and then gradually accumulated in the channels to form nanowires.

Also, a photoreceptor device was fabricated by employing PDD nanowire arrays as the charge generation layer (CGL). It is noteworthy that this n-type semiconductor could show good photoconductivity as well. Our results suggest that the well-defined n-type PDD nanowire arrays can be used as potential building blocks in the construction of hierarchical architectures.

2. Experimental details

2.1. Chemicals

A perylene-diimide derivative (PDD) of pyridine-terphenyl-diimide (see figure 1, top left) was synthesized according to the literature [31] with some modifications. Perylene-3,4,9,10-tetracarboxylic acid dianhydride was reacted with aminopyridine in quinoline (after dehydration with a molecular sieve) via the acylamide reaction by adding a small quantity of zinc acetate as a dehydrating agent. The crude product was

obtained after reaction at 200 °C for 24 h in a N_2 atmosphere, and then purified by repeated washing with ethanol, KOH aqueous solution and deionized water. Finally, the as-prepared product was dried in a vacuum oven overnight. The PDD products, a red powder in nature, show high thermal stability with a decomposition temperature over 500 °C (data not shown here). All other chemicals and solvents were commercially available and used without further treatment.

2.2. Preparation of the AAO templates

Highly ordered and well-aligned AAO membranes were prepared by potentiostatic anodization of high purity Al sheets (0.3 mm thick, 99.99%) in 0.3 M oxalic acid solution using the two-step anodic oxidation method [32, 33]. In order to maintain a constant temperature condition, the anodization was carried out in an ice water bath. The pore diameter and the length of AAO templates could be tailored by changing the anodization time and anodization voltage. The templates used in our study were anodized at 40 V for 2 h. The alumina barrier layer (BL) was reduced by dipping in 5% phosphoric acid at 30 °C for 1 h, and the pore diameter of the AAO membrane was enlarged as well.

2.3. Electrophoretic deposition of PPD nanowire arrays

Electrophoretic deposition was carried out in 40 ml $CHCl_3$ solution containing 10^{-5} M PDD with 0.5 ml of CF_3COOH as the protonating reagent [29]. 30–60 V dc was applied between the AAO/Al and a platinum sheet for 5–60 min, where the Al was used as the cathode and the platinum sheet as the counter electrode. The distance between the two electrodes was kept at 1 cm, and the size of the platinum sheet was about 2.5 cm × 2.5 cm. The length of the PDD nanowires can be controlled at will by changing the electrophoretic deposition time.

2.4. Analysis

The samples for field emission scanning electron microscopy (FESEM) measurement were prepared as follows. The

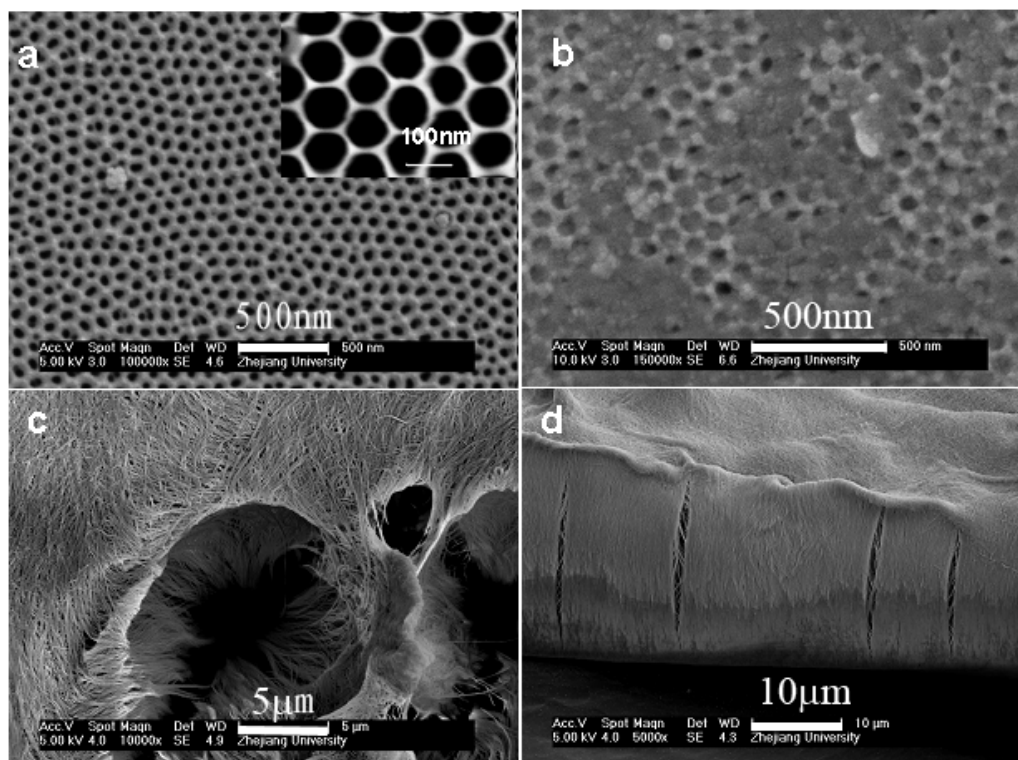


Figure 2. FESEM images of the PDD films by EPD at a potential of 40 V cm^{-1} for 30 min (a) and 60 min (b). Panels (c) and (d) are the top view and side view, respectively, of the PDD nanowire arrays after selectively removing the AAO template from the sample in (b). The inset in (a) shows the morphology of the blank AAO membrane, the pore size of which is about $80 \pm 5 \text{ nm}$.

nanowires formed in the alumina template were uncovered from the top side by immersing the nanostructure-containing AAO membrane into a 10% NaOH aqueous solution for 2–30 min to selectively dissolve the template and by washing with deionized water. Meanwhile, in order to observe the bottom side of the nanowire arrays in contact with the alumina barrier layer on the aluminum substrate, the template with PDD nanowires was first fixed onto a glass plate with epoxy resin, keeping the aluminum substrate upright, then placed into a $\text{CuCl}_2\cdot\text{HCl}$ aqueous solution to remove the aluminum substrate, and finally immersed into a 10% NaOH aqueous solution for 60 min to fully dissolve the AAO template. FESEM images were then taken using a SIRION (FEI) field emission scanning electron microscope with an attachment for an energy-dispersive x-ray microanalysis system (EDAX). For the transmission electron microscopic (TEM, JEM-200CX II) analysis, the nanowires were detached from the glass substrate by sonication in ethanol for a few minutes and one drop of the nanowire suspension was collected on a carbon-coated copper grid.

2.5. Photoreceptor preparation

A double-layered photoreceptor was prepared as follows: the well-ordered and aligned PDD nanowires in AAO templates served as the charge generation layer (CGL), and then a polycarbonate matrix containing 50 wt% phenylhydrazine was coated onto the surface of the CGL as a charge transportation layer (CTL). The resultant film was thoroughly

dried. For a comparison, the photoreceptor employing a cast-coated bulk PDD layer instead of PDD nanowire arrays as the CGL was also fabricated on the aluminum substrate. The photoreceptor configurations were depicted in figure 1 (bottom left, for illustration only; layer thicknesses not in exact proportion to those actually used in this study). The photosensitivity measurement was carried out on a GDT-II model photoconductivity measurement device by a standard photoinduced discharge technique [34, 35], from which a typical photoinduced xerographic discharge curve is given in figure 1 (right). The half-life exposure energy ($E_{1/2}$) is defined as the product of the half-life time ($t_{1/2}$) and the intensity of exposure light (I), that is, $E_{1/2} = I \cdot t_{1/2}$. Photosensitivity (S) is defined as the reciprocal of the half-discharge exposure energy ($S = 1/E_{1/2}$). As can be seen from the discharge curve, a desired photoreceptor should have a large surface potential (V_0), a small residual potential (V_r) and $t_{1/2}$. The larger the S value is, the higher is the photosensitivity of the photoreceptor [30].

3. Results and discussion

3.1. The morphology and structure of PDD nanowire arrays fabricated by the chemical template method

Figure 2(a) illustrates the morphology of the template filled with PDD nanowires by electrophoretic deposition (EPD) at a potential of 40 V cm^{-1} for 30 min. Although the template filled with PDD nanowires is macroscopic red, we could

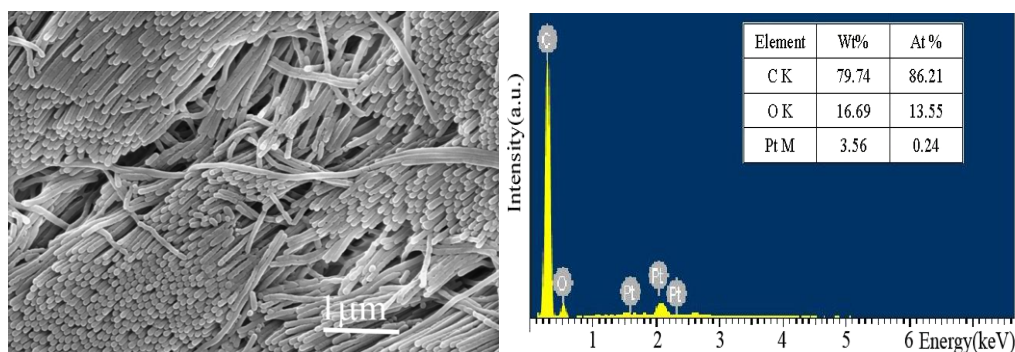


Figure 3. Morphology of the bottom side of the PDD nanowire arrays after fully removing the AAO templates with the top side of the nanoarrays stuck to a glass substrate using epoxy resin (left). The right shows the corresponding EDAX data of the PDD nanowires and the relative percentage of each element.

not clearly see any PDD aggregates on the template surface from the FESEM image, and the pore size exhibits no clear difference compared with that of the blank AAO membrane. By prolonging the electrophoretic deposition time to 60 min, the pores were fully filled by PDD and the surface was quite smooth, as can be seen from figure 2(b). So we concluded that the PDD first deposited at the bottom of the nanochannels of the AAO template and then gradually filled the pores to form longer nanowires. Figures 2(c) and (d) show the top view and side view of the well-aligned PDD nanowire arrays on the aluminum substrate after selectively removing the AAO template. The diameter (d) and the length (L) of the nanowires are about 80 ± 5 nm and $20 \mu\text{m}$, consistent with the internal pore diameters and thickness of the original templates (see the inset in figure 2(a)), respectively. Several studies reported that the nanowire arrays would bend and cluster into disordered domains after the template was removed, due to the surface tension force exerted on the nanowires during the natural drying process in air [36–38]. Although local disorder at the top side of the nanowire arrays induced by the washing and solvent evaporation could be observed, large areas of free-standing and well-aligned nanowire arrays were obtained after removal of the AAO template. Figure 2(d) clearly demonstrated that the nanowires were aligned straight, perpendicular to the substrate and well ordered.

Figure 3 shows the morphology of the bottom side of the PDD nanowire arrays after fully removing the AAO template with the top side of the nanoarrays stuck to a glass substrate using epoxy resin. The nanowires have hemispherical noses and are well aligned over a large area, except for a few irregular nanowires. The corresponding EDAX data of the nanowire arrays demonstrated the components: the C signal was assigned to the PDD and epoxy resin, while the O and Pt signals come from the epoxy resin and the pre-coated conductive Pt film for FESEM measurement, indicating there was no other impurity left in the samples and the template was completely removed.

Figure 4 gives the morphologies of the PDD films by EPD at 40 V for 30 min after selectively removing the template for different immersion times in a 10% NaOH aqueous solution. For a short removing time of 2 min, only the top section of the template was dissolved and no PDD nanowires could be seen

in the top view (figure 4(a)), indicating that the upper section of the template was not filled by PDD. Prolonging the time to 5 min, the template was nearly fully removed with only the barrier layer left. This resulted in the observation of a large area of free-standing nanowire arrays stuck to the barrier layer on the aluminum substrate (figure 4(b)). The nanowires started to collapse and even be detached from the substrates by a longer time for removal of the template (figure 4(c)). The reason is that the barrier layer, the supporter for the nanowire arrays, has been partly dissolved (figure 4(d)). Here, the thin alumina barrier layer acts as the cohesive interlayer between the PDD nanowires and the aluminum substrate. Therefore, all of the results illustrated that the growth of the nanowires in the template nanochannels follows a ‘bottom-up’ growth model, namely, PDD molecules firstly deposited at the bottom of the channels and then filled the channels continuously from the bottom. This growth mode may enable us to prepare free-standing and well-aligned nanowire arrays with tunable lengths by changing the deposition time.

The nanowires were detached from the glass substrate by sonication in ethanol for a few minutes and one drop of the nanowire suspension was collected on a carbon-coated copper grid. Figure 5(a) is the middle section of one single nanowire with a uniform diameter of about 80 nm. The nanowire is straight and has a smooth surface. Although it has been sonicated in ethanol for a long time, the nanowires are still up to several micrometers in length (figure 5(b)), indicating good mechanical stability.

3.2. Photoconductivity study of the PDD nanowire arrays

Photoconductivity of the photoreceptor was evaluated using the standard photoinduced discharge technique, which is the basis of the xerographic process in photocopying systems [39, 40]. As shown in figure 1, the photoconductive process in organic materials consists of three steps: (1) the photoactive material absorbs incident photons and generates excitons in the CGL; (2) the excitons split into electrons and holes; (3) the holes transport through the CTL and subsequently recombine with the static charges on the surface of the CTL. The photoconductivity of the photoreceptors with PDD nanowire arrays as the CGL (PDD-NAs) is given in table 1, accompanied

Table 1. The photoconductivity of the photoreceptors with PDD nanowire arrays as the CGL (PDD-NAs) exposed to illumination. The photosensitivity of the photoreceptors from the bulk PDD (PDD-bulk) film is also given for comparison.

No.	V_0 (V)	V_r (V)	R_d ($V s^{-1}$)	$t_{1/2}$ (s)	$E_{1/2}$ ($mJ cm^{-2} s$)	S ($cm^2 mJ^{-1} s^{-1}$)
PDD-bulk	179	17	50	4.01	4.411	0.2267
PDD-NAs	175	7	14	0.41	0.451	2.217

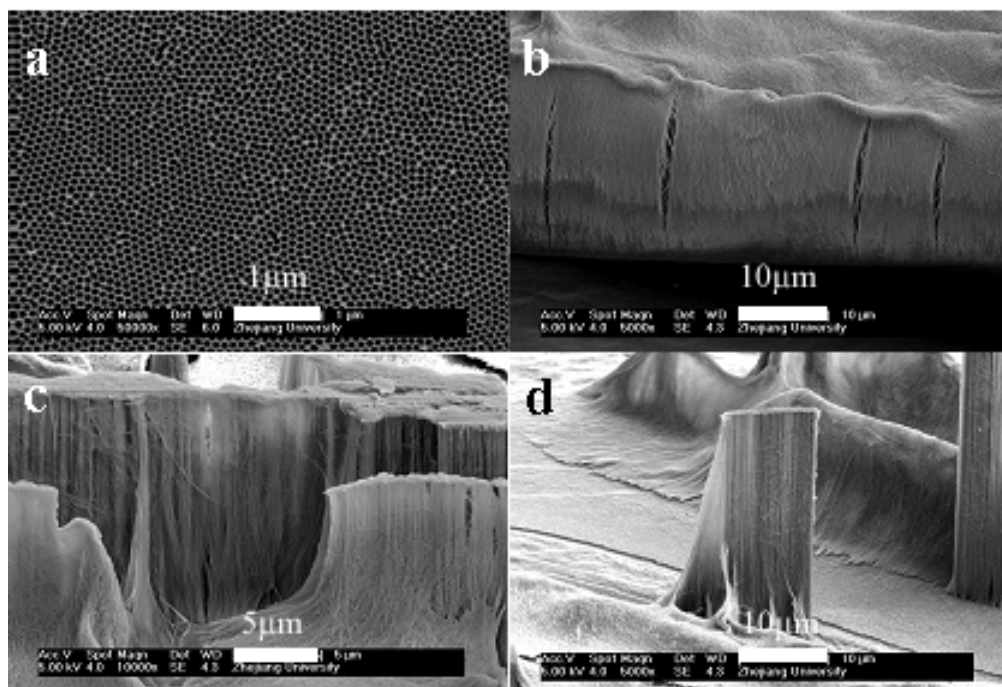


Figure 4. Morphologies of the PDD films by EPD at 40 V for 30 min after removing AAO templates in a 10% NaOH aqueous solution for 2 min (a), 5 min (b) and 10 min ((c)–(d)).

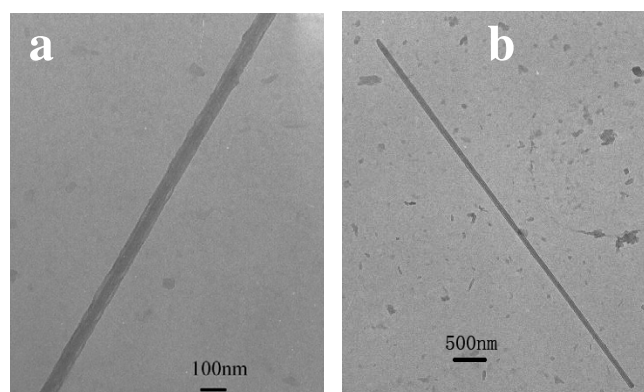


Figure 5. TEM images of a section of one single PDD nanowire with the diameter of about 80 nm (a) and one entire straight nanowire with the length of several micrometers (b).

by the photoconductivity of their bulk counterparts (PDD-bulk) for comparison. It should be noted that, since minor variations in performance parameters are natural across devices within one set due to imperfect controllability, the performance parameters reported herein are representative of the best case of photosensitivity across each set.

As can be seen from table 1, when exposed to light with an intensity of $1.1 mJ cm^{-2}$, the photoreceptor from the

bulk PDD (PDD-bulk) has a photosensitivity with a $t_{1/2}$ of 4.01 s and a S of $0.2267 mJ^{-1} s^{-1} cm^2$. The photoreceptor of PDD-NAs shows a good photoconductivity with a residual potential (V_r) of 14 V, a half-life time ($t_{1/2}$) of 0.41 s and a photosensitivity (S) of $2.217 mJ^{-1} s^{-1} cm^2$, nearly one magnitude greater compared to that of the bulk PDD sample. This improvement is believed to be induced by the larger interfacial areas and the one-dimensional (1D) continuous charge carrier channels in the PDD nanowire arrays, which are out of reach in the bulk samples. It is noteworthy that we have measured the photoinduced xerographic discharge curve of the photoreceptors with the PDD nanoarrays in the templates by EPD at 40 V for 30 min, where PDD nanoarrays are not fully filled in the AAO template. It is found that this photoreceptor cannot be discharged and shows no photoconductivity. This can easily be understood from the fact that the charge carrier transport is interrupted, because the nanowires were not longer enough to contact the charge transport layer as shown in figure 2(a).

It was found that the initial surface potential V_0 of the photoreceptor was very low, below 200 V. Three reasons may explain this phenomenon. Firstly, the PDD has a high electron transportation capability and the charged electrons can move back to the conductive substrate and discharge there. Secondly, since the nanoarrays were directly grown on the

electrically conductive aluminum substrates, we could not insert a insulating interface layer of polyamide or PMMA as a block layer for charge carriers, which is a well-known method for increasing the V_0 [41, 42]; but it is fortunate that the bulk alumina barrier layer at the bottom of the nanochannels can make some compensation for the lack of an insulating layer. Finally, the photoconductivity mechanism of the PDD, as one of the n-type semiconductors, may have its own exceptional character different from previous research on p-type semiconductors.

4. Conclusion

In summary, we have fabricated well-defined and highly ordered PDD nanowire arrays with AAO templates via the electrophoretic deposition method. After removing the templates, the uncovered nanowire arrays were free-standing and vertical to the substrate. The lengths and diameters of the as-prepared PDD nanowires can be easily controlled by using different pore sizes and film thicknesses of the AAO templates. We also found that the growth process of the PDD nanowires in the nanochannels of AAO templates followed a 'bottom-up' growth model, which enables us to facilely control the lengths of the nanowire arrays by varying the deposition time. The performance of the photoreceptor with the PDD nanowire arrays as the CGL shows that the photosensitivity is one order of magnitude higher than that of the cast film of bulk PDD as the CGL. This study demonstrated that highly ordered and well-aligned n-type PDD organic nanowires show much better performance on photoconductive devices than bulk materials, which could find many other applications such as photovoltaic cells, organic lasers, etc.

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