Well-defined perylene- diimide nanowire arrays fabricated via template method and their photoconductivity

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Abstract

Well-defined one dimensional (1D) organic nanowire arrays were prepared by introducing one Perylene-Diimide derivative (PDD) into AAO templates via a simple electrophoretic deposition method. The morphology of as-deposited films was investigated by field emission scanning electron microscope (FESEM). The resulting nanowires are highly-ordered after removing the AAO supporters. The photoreceptor with the PDD nanowire arrays as the charge generation layer (CGL) exhibits better photosensitivity than their bulk counterparts under light illumination, indicating potential applications in the area of photoimaging process.

1. Introduction

Fabrication of nanometer-scale components in desired geometries is significant for the new generation of optics, electronics, and other area [1-3]. In particular, highly-ordered and vertically-aligned nanowire arrays with a high aspect ration on the conductive substrate are expected to have high charge carrier mobilities because of their well-defined transportation channels for carriers [4].

Perylene bisimides are one of the most thoroughly studied classes of organic semiconductors with many potential applications such as fluorescent solar collectors, photovoltaic cells, and dye lasers[5-7]. Because they have not only outstanding chemical, thermal, and photochemical stability, but highly absorbing in the visible to NIR region and emit fluorescence with quantum yields near unity[8, 9], so to construct well-ordered and aligned Perylene bisimide nanowires is of significance from both a fundamental and a particular point of view. However, so far as we know, it is still a challenge that how to obtain highly ordered nanowire array structure by using a facile and controllable fabrication technique.

Due to the convenience in controlling the size of as-prepared nanowires, especially the diameter, template-synthesis-method has proved to be a versatile approach for nanomaterials preparation [10, 11].

In this paper, we successfully fabricated the well-aligned and vertically-oriented Perylene-Diimide derivative (nominated as PDD below, and the structure is given in chart 1) nanowire arrays against conductive substrate via a simple electrophoretic template technique. Furthermore, a photoreceptor was made of PDD nanowire arrays, which shows enhanced photosensitivity compared to that of its bulk counterparts.

2. Experimental

2.1. 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 two-step anodic oxidation method [12] with some modifications.

2.2. Electrophoretic deposition of the PPD nanowire arrays

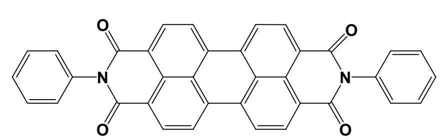
Electrochemical deposition was carried out in a $CHCl_3$ solution containing 10^{-5} M PDD with 0.5 mL of CF_3COOH as the protonating reagent [13] at 30-60 V dc applied between the AAO/Al with Al as the cathode and a platinum sheet as the counter electrode for 5–60 min.

2.3. Analysis

The preparation method of the samples for field emission scanning electron microscopy (FESEM) measurement was as follows: the 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. FESEM images were then taken using SIRION (FEI) field emission scanning electron microscope with an attachment of an energy dispersive X-ray microanalysis system (EDAX). UV-vis absorption spectra were recorded on a CARY Bio100 spectrophotometer. X-ray diffraction (XRD) analysis was performed on a Rigaku D/max diffractometer with Cu Kα radiation.

2.4. Photoreceptor preparation

A simple 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 polycarbonate matrix containing 50 wt% phenylhydrazone was coated on the surface of CGL as a charge transportation layer (CTL). The resultant film was thoroughly dried. For a comparison, the photoreceptor employing 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 Chart 1. The photosensitivity measurement was carried out on a GDT-II model photoconductivity measuring device by a standard photoinduced discharge technique [13], where the bigger the photosensitivity (S) is, the better the photoconductivity of the photoreceptor is.



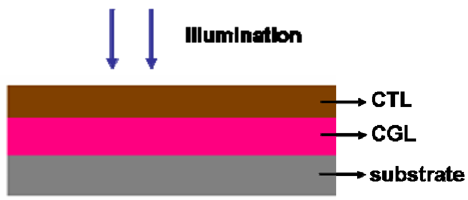
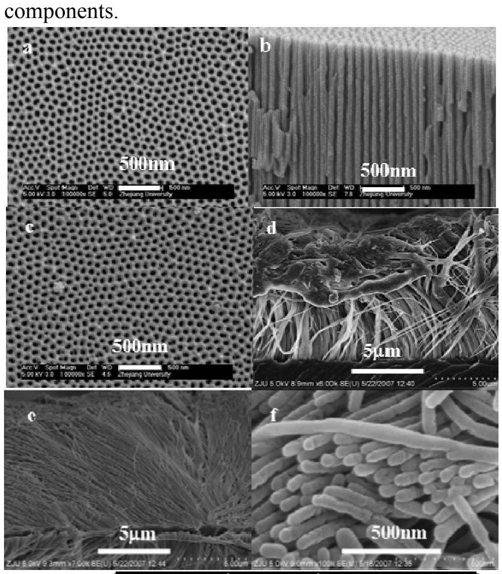


Chart 1. The structure of PDD molecule (upside) and the schematic structure of the dual-layered photoreceptor using PDD nanowire arrays as the charge generation layer (underside).

3. Results and discussion

3.1. The morphology and structure of PDD nanowire arrays

Figure 1a and 1b respectively give the top view and side view of the template used in this work. The AAO membrane were uniform size and took a high order arrangement with honeycomb hexagonal structure, with the average diameter and the length of the template of about 80 nm and 20 μm, respectively. As can be seen from Figure 1c, by electrophoretic deposition (EPD) at a potential of 40 V/cm for 30min, the pores were not fully filled by PDD and the surface was very similar to the blank AAO membrane in Figure 1a. However, the pores of the AAO membrane can be fully filled by PDD after EPD for 60min (data not shown here). Figure 1d and figure 1e give the side view and top view of the well-aligned PDD nanowire arrays on aluminum substrate after selectively removing the AAO template. The diameters (D) and lengths (L) of nanowires are about 80±5 nm and 20 μm, consistent with the internal pore diameters and the thickness of original templates, respectively. Although local disorder at the top side of the nanowire arrays induced by the wash and solvent evaporation could be observed, large area of well-aligned nanowire arrays were obtained after removal of the AAO template. Fig. 1f demonstrated the ordered and well-aligned morphology of the PDD nanowires grown from the membrane under high magnification. The corresponding EDAX data for the nanowire arrays in Figure 1e demonstrated the components.



Element	Wt%	At%
C K	51.77	66.08
O K	16.72	16.02
AlK	31.51	17.90

***Figure 1.** The morphologies of the AAO membrane from the top view a) and side view b), respectively. For a short EPD time, the template pores were not fully filled by PDD nanowires. By selectively dissolving the AAO templates, the PDD nanowires were free-standing on the substrate d) and showed uniform diameter. An FESEM iamge with high magnification is given in f). The corresponding EDAX data for the nanowires in e) demonstrate the PDD component of the nanowires.*

3.2. Optical property and crystal structure of the PDD nanowire arrays

The UV-vis spectroscopy is given in Figure 2a. The PDD nanowires without AAO supporter show a strong and broad absorption band in the range from 400-600 nm, with two absorption peaks at about 498 nm and 534 nm, accompanied with a shoulder peak near 465 nm. Another absorption peak appears around 370 nm. The X-ray diffraction patterns for the PDD nanowires (see Figure 2b) give several diffraction peaks, demonstrating that the PDD nanowires are polycrystalline.

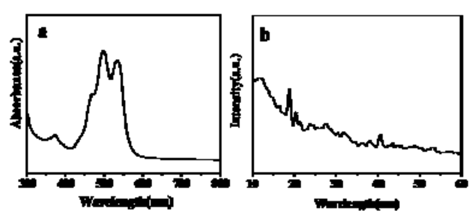


***Figure 2.** UV-vis spectroscopy a) and the XRD patterns b) of the PDD nanowire arrays by electrophoretic deposition into the AAO pores at 40 V/cm for 60 min, and the AAO membrane has been removed with 10% NaOH aqueous solution for the measurement.*

3.3. Photoconductivity of the PDD nanowire arrays

The photoconductivity of the photoreceptors with PDD nanowire arrays （the same with Figure 1） as CGL before (No. PDD) and after thermal (No. PDD-T) treatment is given in Table 1, with the photoconductivity of their bulk counterparts (PDD-bulk) as a comparison.

We can see that when exposed to the light with the intensity of 1.1 mJ/cm^2, the photoreceptor of the PDD nanowire arrays shows a good photoconductivity with the residual potential (V_r) of 39 V, the half-discharge time ($t_{1/2}$) of 3.27 s, and the photosensitivity (S) of 0.2780 (mJ s)$^{-1}$cm^2. As comparison, the photoreceptor from the bulk PDD (PDD-bulk) has a worse photosensitivity with the $t_{1/2}$ of 4.01 s, and the S of 0.2267 (mJ s)$^{-1}$cm^2, lower than that of the PDD nanoarrays. The improved photoconductivity for PDD nanowire arrays in the AAO channels over their bulk counterparts is believed to be induced by the large interfacial areas and the one-dimensional (1D) continuous charge carrier channels in the PDD nanowire arrays. It is noted here we have measured the photoinduced xerographic discharge curve of the photoreceptors with the PDD nanoarrays in the templates by EPD at 40 V below 60min and find that they can't discharge and show no photosensitivity. It can easily be understood from that the charge carrier transport is interrupted due to the hollow pores near to the template surface showed in Fig. 1c. Moreover, the photosensitivity of the as-prepared PDD nanowire arrays could be further improved by annealing treatment at 100°C for 12 h. As can be seen from table 2, the photosensitivity of the anneal PDD nanowire arrays (PDD-T) shows a S value of 2.217 (mJ s)$^{-1}$cm^{2}, about four folders higher than that of the PDD nanowire arrays without any thermal treatment, and nearly six times of the photosensitivity of the bulk PDD. We reasoned that the poorer crystalline state of the PDD nanowires without any thermal treatment, the residual solvents in the nanochannels and absorbent gas impurity would reduce the photosensitivity of the photoreceptor. Some advisable anneal treatment within the thermal stability range of the photoreceptor could improve the local crystalline of the nanowires and remove the residual solvent and other gas impurities, which therefore enhances the photosensitivity of the photoreceptor.

Table 1. The photoconductivity of the photoreceptors with PDD nanowire arrays as CGL before (No. PDD) and after (No. PDD-T) thermal treatment exposed to illumination with the intensity of 1.1 mJ/cm^2. The photosensitivity of the photoreceptors from the bulk PDD film is also given for comparison.

No.	V_0 (V)	V_r (V)	R_d (V s^{-1})	$t_{1/2}$ (s)	*S* (cm^2 mJ^{-1} s^{-1})
PDD-bulk	179	17	50	4.01	0.2267
PDD	140	39	9	3.27	0.2780
PDD-T	132	15	10	0.69	1.3175

4. Conclusion

In summary, we have fabricated well-defined and highly-ordered PDD nanowire arrays with AAO templates via the electrophoretic deposition method.

The photoreceptor with the PDD nanowire arrays in the AAO template shows better photosensitivity compared to that of the cast-film of bulk PDD on the aluminum substrate, and their photosensitivity can be further improved by anneal treatment. In brief, this study directly illuminated that, highly-ordered and well-aligned one dimensional organic nanowires facilely prepared by AAO template method manifest their much better performance on photoconductive devices than that of bulk materials, which could be expected to extend to a wider application like photovoltaic cells.

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Ru Bai studied as a PHD candidate in Zhejiang University (2003 ~). Her work has mainly focused on the preparation and characterization of the ordered composite optoelectronic functional nanomaterials for optoelectronic devices.