Chapter 51
Deposition of Perylene Diimide Derivatives for Dye-Sensitized Solar Cells

N. Georgiev, H. Nichev, M. Petrov, K. Lovchinov, D. Dimova-Malinovska, and V. Bojinov

Abstract The aim of this work is to examine the photosensitivity of dye-sensitized materials. Three types of organic dye sensitizers, i.e. perylene diimide (PDI) derivatives with different terminal groups were synthesized. The synthesized PDI derivates were deposited by dipping on a glass/ITO substrate covered with arrays of ZnO nanorods (NR) grown by an electrochemical process. An Ag grid contact was deposited on the PDI films on the stack glass/ITO/ZnONR/PDI; then I-V characteristics of the structures were measured in dark and under illumination with a halogen lamp. The photosensitivity of the different dye-sensitized materials is discussed.

Keywords Photoconductivity • Perylene diimide derivatives • ZnO nanorod arrays

51.1 Introduction

The main efforts in the photovoltaic (PV) technology are focused on increasing the efficiency and decreasing the price of the solar cells and modules. Solar cells on perylene diimide derivatives (PDI) have attracted the interest of researchers as an alternative to the high cost Si solar cells. The synthesis and the study of the characteristics of these materials are of high importance for the fabrication of solar cells. The increased interest in solar cells based on organic materials is due to their advantages: a potential low cost thin film PV technology, low toxicity, technological merits in producing photoconductive compositions, and the possibility of deposition of large area substrates.

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For the last 10 years increasing efforts have been devoted to the development of organic sensitizers, and reasonable photo-conversion efficiencies have been reached with some push-pull type organic chromophores. The representatives of these materials are perylene diimide derivatives owing to the unique outstanding chemical, thermal and especially photochemical stability.

The reduction of the dimensions of materials to a nanometer scale gives rise to several advantages in terms of device applications. Nanomaterials such as nanowires and nanorods have unique advantages that make them useful in photovoltaic devices [1]. Nanostructured materials can be produced by non-vacuum technologies on large area substrates. All these advantages offer the possibility to increase the efficiency of solar cells and modules and to reduce their costs. Layers of nanostructured arrays can be deposited with very large surface area per unit volume and offer a possibility to improve light trapping properties of solar cell due to the rough interface with increased effective areas between the films.

The photovoltaic devices based on inorganic semiconductor such as ZnO with vertically oriented nanowire and nanorod structure [2] have been applied as anti-reflecting coating (ARC) in Si heterojunction solar cells [3] and used as substrates for a-Si:H thin film solar cells [4] with improved efficiency. ZnO nanorod arrays have been integrated in organic photo-active materials, as well [2, 5, 6].

In this work we report on the preparation of three types of PDI layers on ZnO nanorod arrays grown by electrochemical process on glass/ITO substrates via dip-ping in a solution. An Ag grid contact was deposited on the structure glass/ITO/ZnO NR/PDI, and I-V characteristics of the structures were measured in dark and under illumination with a halogen lamp for assessment of their photosensitivity.

51.2 Experimental

The three types of perylene diimide derivatives (PDI) were synthesized on the base of the perylene diimide derivatives (1 in Fig. 51.1). P.a. grade N, N-dimethylethylenediamine, ethylenediamine, methyl acrylate and perylene-3,4,9,10-tetracarboxylic (Aldrich) were used without purification. All solvents (Aldrich, Fisher Chemical) used for the process of synthesis were pure or of spectroscopy grade.

The properties of the synthesized PDIs were evaluated by FTIR, UV-VIS and fluorescence spectroscopy. FTIR spectra of were recorded with a Varian Scimitar 1000 spectrometer. UV-VIS absorption spectra were recorded with a spectrophotometer Hewlett Packard 8452A. Fluorescence spectra were taken with a Scinco FS-2 spectrofluorimeter at room temperature (25 °C). The relative fluorescence quantum yield Φ_F was determined using Coumarin 6 (Aldrich, $\Phi_F = 0.78$ in ethanol [7]) as a standard. The I-V characteristics of the structures glass/ITO/ZnO NR/PDI/Ag grid were measured using a Keithley 2400 Source Meter in dark and under illumination by a halogen lamp in order to study their photosensitivity.

51.3 Results and Discussion

51.3.1 Synthesis of PDI 2 and PDI 3

The dyes PDI 2 and PDI 3 were synthesized using by the consecutive refluxing a suspension of 2 g (5 mmol) perylene-3,4,9,10-tetracarboxy anhydride (1 in Fig. 51.1) and N,N-dimethylethylenediamine or ethylethylenediamine in water/propanol. 2.1 ml of the primary amine N,N-dimethylethylenediamine was added to obtain PDI 2 or 2 ml ethylenediamine to obtain PDI 3. Additionally, a mixture of 50 ml water and 50 ml n-propanol was added.

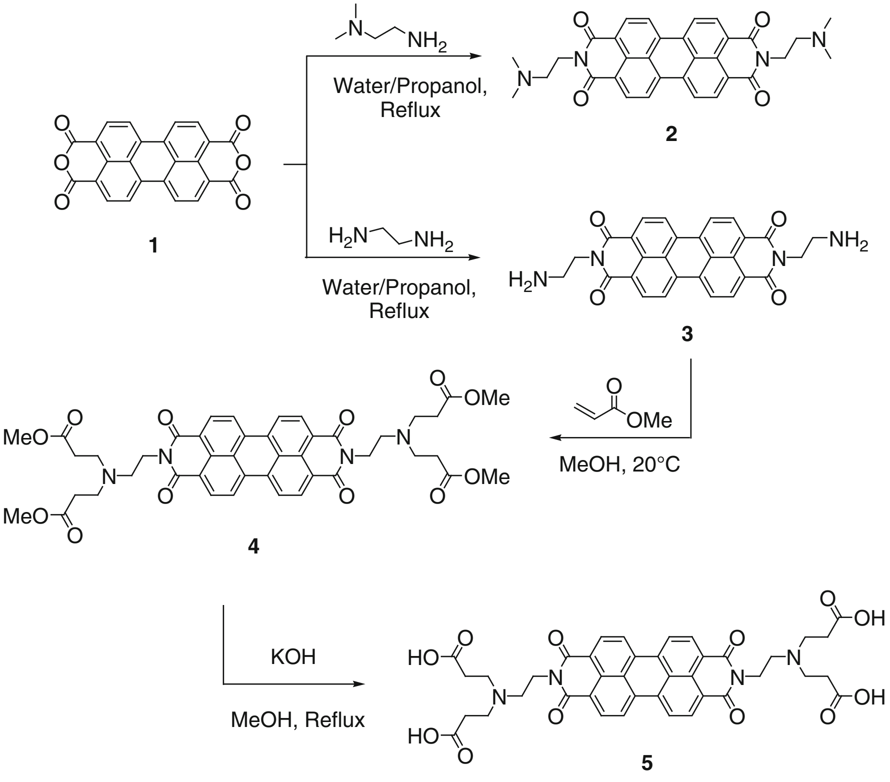

Fig. 51.1 Scheme of the procedure of the synthesis of PDIs

The resulting mixture was heated at 90 °C under reflux for 4 h. After cooling to room temperature the precipitate was collected by filtration, washed with water and dried. Then the obtained solid powder was treated with 100 ml of 5 % aqueous solution of sodium hydroxide to give the pure compounds after filtration, washing with water and drying. The results of analyses show:

- PDI 2: Yield = 2.4 g (91 %). IR (KBr) cm^{-1}: 2,962 and 2,770 (νCH); 1,694 (ν_{as}N-C=O); 1,658(ν_sN-C=O). Elemental analysis: Calculated for $C_{32}H_{28}N_4O_4$ (MW 532,6): C 72.16, H 5.30, N 10.52 %; measured: C 71.89, H 5.22, N 10.85 %.
- PDI 3: Yield = 2.2 g (94 %). IR (KBr) cm^{-1}: 3,352 (νNH2); 1,696 (ν_{as}N-C=O); 1,659 (ν_sN-C=O). Elemental analysis: Calculated for $C_{28}H_{20}N_4O_4$ (MW 476,5): C 70.58, H 4.23, N 11.76 %; measured: C 70.83, H 4.17, N 11.47 %.

51.3.2 Synthesis of Perylene-3,4,9,10-Tetracarboxylic Diimide (PDI 4)

The synthesis of the novel perylene tetracarboxydiimide PDI 4 is shown in Fig. 51.1. The dye PDI 4 was synthesized via a divergent strategy, involving initial Michael-addition of the aminofunctional core PDI 3 with methyl acrylate. The structure and purities of the prepared products were confirmed by conventional techniques (elemental analysis, UV-VIS, fluorescence and FTIR spectroscopy).

A mixture of methyl acrylate (2.7 ml, 32 mmol) and 1.5 g of PDR 3 (3.2 mmol) in 30 ml methanol was stirred for 4 days at room temperature, then the precipitate was collected by filtration, washed with water and dried. Then the crude solid was extracted with boiling chloroform to give, after vacuum evaporation of the solvent and silica-gel chromatography in CH_2Cl_2, pure PDI 4 as dark-red crystals (melting point 206–209 °C). The results of the analyses were:

- PDI 4: Yield = 0.74 g (28 %). IR (KBr) cm^{-1}: 1,730 ($nCOOCH_3$); 1,688 (ν_{as}N-C=O); 1,660 (ν_sN-C=O). Elemental analysis: Calculated for $C_{44}H_{44}N_4O_{12}$ (MW 820.9): C 64.38, H 5.40, N 6.83 %; measured: C 63.19, H 4.99, N 6.70 %.

51.3.3 Synthesis of Perylene-3,4,9,10-Tetracarboxylic Diimide (PDI 5)

PDI 5 was obtained by conversion of PDI 4 by hydrolysis. A suspension of PDI 4 (0.5 g, 0.6 mmol) in EtOH (15 mL) was added to NaOH (0.25 g, 6.3 mmol) and dissolved in hot EtOH (20 mL). The mixture was heated to reflux for 12 h. The precipitated crude product was filtered off after cooling, washed with water and dried. Silica gel chromatography yielded 0.24 g of PDI 5. The results of analyses were:

- PDI 5: – Yield = –0.24 g (53 %). IR (KBr) cm^{-1}: 3,052 (nOH); 1,669 and 1,681 (νN-C=O). Elemental analysis: Calculated for $C_{40}H_{36}N_4O_{12}$ (MW 764.7): C 62.82, H 4.74, N 7.33 %; measured C 62.52, H 4.49, N 7.44 %

The IR spectra of the prepared perylene diimides PDI 2 to PDI 5 show two absorption bands in the range 1,650–1,690 cm^{-1} resulting from the presence of the imide ring. No absorption bands above 1,750–1,800 cm^{-1} corresponding to anhydride carbonyl group absorptions were observed. This is evidence that the starting perylene anhydride (1) was completely converted to the perylene diimides PDI 2–5.

The dyes under investigation are based on the same chromophoric system, thus their absorption spectra are identical. In dimethyl formamid (DMF) solution the examined PDIs demonstrate UV-vis absorption spectra typical for perylene tetracarboxydiimide [8] with three pronounced peaks at 460, 490 and 526 nm which corresponds to the 2–0, 1–0 and 0–0 electron transitions, as the highest intensity was observed for the lowest energy band.

The synthesized PDIs are based on the “fluorophore-spacer-receptor” model, where the perylene diimides core is the fluorophore and the tertiary amines are the receptors. For these particular cases it was predicted that a photoinduced electron transfer (PET) from the receptor to the excited state of the fluorophore would quench fluorescence emission of the PDI unit [9]. This is why the dyes PDI 2, 4 and 5 show extremely low fluorescence with quantum yields in range between 0.005 and 0.008. We chose the PET based PDIs as dye sensitizers since the PET process stabilizes the excited dye state and favours the charge separation.

The correct design of the binding groups plays a critical role to prevent aggregation of the chromophores and to tune the properties of the dye layer. It is well known that carbonyl derivatives are suitable linkers for different metal oxides [10]. That is why the dyes PDI 4 and PDI 5 are ester and carboxylic acid terminated, respectively. Compound PDI 2 which lacks a linker group was introduced in the present study in order to receive a more complete comparative picture for the influence of the dye terminal groups.

51.3.4 Deposition of ZnO Nanorods Arrays

ZnO layers were deposited by mean of an electrochemical process in an aequeous solution of $ZnCl_2$ and KCl using a electrochemical three-electrode cell with a saturated calomel electrode (SCE) as reference electrode [11]. The electrolyte contents $ZnCl_2$ (5×10^{-4} M) and KCl (1 M) with pH ~ 5. The deposition temperature was 80 °C. The deposition was carried out controlling the potential by a high power potentiostat system WENKING HP 96. Since the potential of Zn in the electrolyte is −1.05 V vs. SCE, the deposition process of ZnO was carried out at −1.0 V vs. SCE to prevent deposition of metallic Zn. Good quality ZnO films were obtained at a redox potential within the range between +0.30 and +0.40 V vs. SCE. At a redox potential higher than +0.4 V zinc peroxide (ZnO_2) was formed on the samples with a poor adhesion to the substrate. A spectrally pure graphite plate was used as an anode. The electrolyte was agitated by a magnetic stirrer. ITO on glass was used as conductive substrate for the growth of ZnONR [12]. The growth time was 20 min. The deposition of thin ZnO films at a redox potential lower than +0.4 V can be explained as a product of the interaction of OH^- and Zn^{2+} on the surface of the electrode [13].

$$Zn^{2+} + 2OH^- \rightarrow Zn(OH)_2 \rightarrow ZnO + H_2O$$

After deposition of the ZnO layers on the glass/ITO substrates they were cleaned with acetone. For coating with the PDIs the cleaned substrates was immersed into a dye solution in DMF (dye concentration 1×10^{-5} mol/L), kept for 24 h and then dried in air.

51.3.5 *I-V Measurements*

An Ag grid contact was deposited on the structure glass/ITO/ZnO NR/PDI (Fig. 51.2). The Ag contact was deposited on the ITO layer. The photocurrent was measured between the Ag metal electrode on the ITO and the front Ag grid electrode in dark and under illumination by light from a halogen lamp (−900 W) on the side of the Ag grid. The positive potential was applied to Ag electrode deposited on ITO.

The I-V characteristics in dark and under illumination are presented in Fig. 51.3. The I-V characteristics of the structures with PDI 2 and 4 demonstrate a rectifying effect. The structures with the three different PDI under investigation demonstrate photosensitivity. The structure with PDI 4 possesses the highest photosensitivity. In this case the dye is Probably deposited as monolayer on the surface of the ZnO NR which results in a decrease of the recombination of the carriers genarated by the light.

The synthesized dye PDI 2 demonstrates a lower photosensitivity probably because it possesses no anchor groups which could help to bind the PDI on the

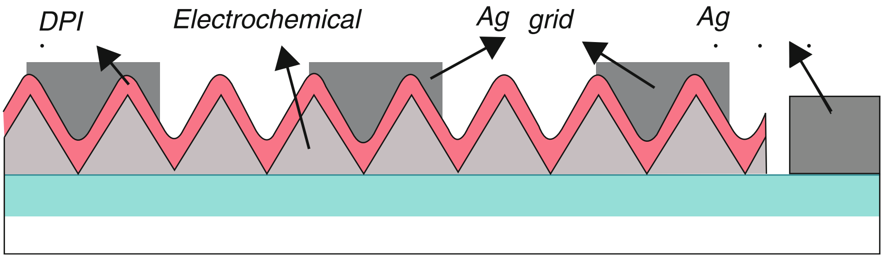

Fig. 51.2 Scheme of the structures with ZnO NR arrays and PDI derivatives for I-V measurement

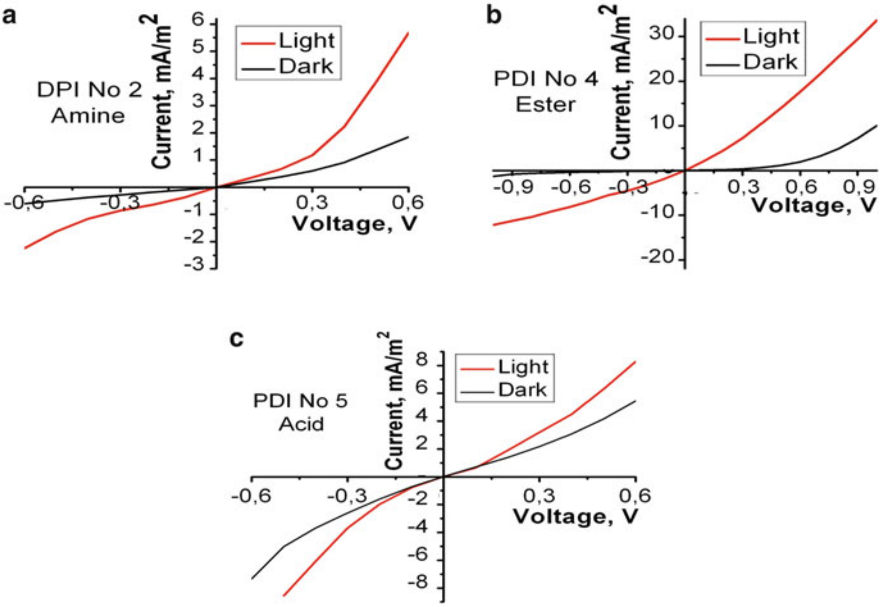

Fig. 51.3 I-V a characteristics of the structures glass/ITO/ZnO NR/PDI/Ag grid in *dark* and under illumination for PDI 2 (**a**), PDI 4 (**b**) and PDI 5 (**c**)

rough nanostructured ZnO surface. The samples with PDI 5 shows a very weak photosensitivy. Due to the poor solubility the synthesized dye forms very easily aggregates, which prevent formation of a homogeneous continuous PDI film; thus it is necessary to apply high voltages to obtain a photo-current.

51.4 Conclusions

In this work it was shown that perylene diimide derivatives with different terminal groups can be synthesized using perylene-3,4,9,10-tetracarboxy anhydride by adding different primary amines. The synthesized PDI derivatives were deposited on the surface of ZnO nanorod arrays grown by an electrochemical method on conductive glass/ITO substrate. The photosensitivity of the structure ITO/ZnO NR/PDI/Ag grid was studied. The PDI 4 (ester terminated) demonstrated the highest photosensitivity probably as a result of the formation of a monolayer which impedes carrier recombination.

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