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Solution-Processed Polyfluorene:Naphthalenediimide–N-Doped TiO_2 Hybrids for Ultraviolet Photodetector Applications

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In this study, highly efficient ultraviolet (UV) photodetectors based on a solution-processed system are introduced. Nitrogen-doped TiO_2 nanoparticles are embedded in poly(9,9-dioctylfluorenyl-2,7-yleneethynylene) (PFE):*N*,*N'*-bis-*n*-butyl-1,4,5,8-naphthalenediimide (BNDI) (3:1 wt.%) blends. An UV-active layer of [(PFE:BNDI)(3:1):ammonium hydroxide-TiO_2] [9:1 wt.%] gave a photoresponsivity value of 545 ± 6.92 mA/W at -4 V under 1 mW/cm^2 UV light at 365 nm, and this value was increased to 597 ± 9.22 mA/W on annealing the active layer at 60°C. The efficiencies obtained are strongly dependent on the nitrogen source nature, their donor–acceptor relationship, and the morphological interaction with the PFE:BNDI blend.

Key words: Ultraviolet photodetector, hybrid system, conjugated polymer, N-doped TiO_2

INTRODUCTION

During the last decades, use of organic semiconductors in photonic applications has attracted great attention in the literature.[1–11] The main reasons for this are the relatively low investment requirements and greater material variety of organic semiconductor technology. Besides other photonic applications, organic semiconductors have become popular due to their sensitivity and selectivity in visible–near infrared,[12–14] infrared,[15–17] and ultraviolet (UV) sensing applications.[1,3,18–21] Although UV radiation covers a relatively small region of the solar spectrum, its biological effects are important.[22] Depending on the biological effects, the UV region is subdivided into three spectral bands: UVA (320 nm to 420 nm), UVB (280 nm to 320 nm), and UVC (100 nm to 280 nm).[23] While UVC radiation is completely and UVB radiation is partially absorbed by the atmosphere, UVA reaches the Earth's surface by diffuse or direct solar radiation.[24] The literature contains many valuable studies on assessment and/or monitoring of UV radiation.[22,24–30]

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Wide-bandgap inorganic semiconductors such as GaN,[26] ZnO,[25,27–29] and TiO_2[30] are widely acknowledged in UV photodetector (PD) applications. Although their organic counterparts still have some problems in terms of responsivity, they have started to become serious alternatives.[21] During the last few years, reports on metal oxide–organic hybrid systems that attempt to combine the advantages of both types of semiconductors have been published (Table I).[31–37]

TiO_2 is one of the most studied *n*-type semiconductors, and the advantages of nitrogen (N)-doped TiO_2 for light-harvesting applications are widely known.[38–40] In our previous studies, we reported quite a high responsivity, i.e., 410 mA/W at -4 V under 1 mW/cm^2 at 365 nm, from an indium doped tin oxide (ITO)/poly(3,4-ethylenedioxy thiophethiophene) (PEDOT):poly(styrene sulfonate) (PSS)/poly(9,9-dioctylfluorenyl-2,7-yleneethynylene) (PFE):*N*,*N'*-bis-*n*-butyl-1,4,5,8-naphthalenediimide (BNDI) (3:1)/Al PD device structure,[21] and increased the light-harvesting ability of TiO_2 by amine doping.[41] Nonetheless, to the best of our knowledge, use of N-doped TiO_2 nanoparticles in organic UV PDs has not been reported in the literature.

In this work, dipropylamine (DPRYL)-, ammonium hydroxide (NH_4OH)-, and diethanolamine (DETOH)-doped TiO_2 nanoparticles in 1:1 mol ratio[41] are employed in the active layer of a UV PD. The PD