



High efficient UV-A photodetectors based on monodispersed ligand-capped TiO₂ nanocrystals and polyfluorene hybrids

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ABSTRACT

Monodispersed ligand-capped TiO₂ nanocrystals are synthesized by a low temperature solvothermal method using oleic acid (OA) as the capping agent. The single layer hybrid films based on the OA-capped TiO₂ nanocrystals and poly(9,9-dihexylfluorene) (PFH) are prepared by solution processing at room temperature and characterized by atomic force microscopy, UV–vis absorption and photoluminescence spectra. The hybrid film is applied in the fabrication of nanostructured UV-A photodetector (320–420 nm) by sandwiching it between two electrodes to form bulk heterojunction. The high ultra-violet signal-to-noise ratio of 3 orders of magnitude with short response time less than 200 ms can be achieved for the device. Furthermore, the device shows drastic changes in current under a wide range of UV irradiation with a linear relationship between them. The thermal behavior of the device is also discussed. The high photosensitivity in the UV-A range and the low-cost endow them with potential for environmental and biological uses.

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1. Introduction

In recent years, ultraviolet (UV) photodetectors have drawn much attention for their civil and military uses such as solar UV monitoring, flame sensors, UV communication, space research, and so on [1–3]. According to the common classification of UV light with respect to the wavelength, only the longest wavelength of the UV-A range (320–420 nm) can reach the Earth's surface. The UV-B light (280–320 nm) and the UV-C light (200–280 nm) can be completely absorbed by the molecules in sunscreen lotions and the molecules in the Earth's atmosphere, respectively, not allowing them to reach the ground [4]. Since the UV-A light may cause some diseases such as a skin cancer, developing novel UV-A photodetectors with high sensitivity to the UV-A light becomes more and more important.

Most of the UV-A detectors are made of inorganic semiconductors such as doped GaN [5], ZnO [6], and TiO₂ [7,8] due to their wide bandgap, fast response time, higher response, and stability. However, they are constructed on expensive substrates such as sapphire, and the related fabrications are troublesome and costly, which limit their large-scale applications. Besides the inorganic systems, organic UV-A detectors have undergone rapid

development recently. Compared to their inorganic counterparts, organic photodetectors are considered as a complementary for the advantages of simple fabrication processes, lighter weight and lower cost [9]. Their performance, however, is worse than the inorganic ones [10]. However, Lin et al. reported organic UV photodetectors consisting of large bandgap triaryldiamine and oxadiazole-containing oligoaryls as the efficient electron-transfer donor–acceptor couple, which have comparable efficiencies to a commercial UV-A photodetector made of GaN and cover the whole UV-A range [11]. Compared with the pure inorganic or organic devices, the organic/inorganic hybrid devices, combining the advantages of each component and overcoming their disadvantages, usually indicate obvious superiority [12–14]. UV-A detectors applying poly(9,9-dihexylfluorene) (PFH) and ZnO nanorods arrays were recently reported by Lin et al. [15]. Yamaura et al. [16] fabricated PEDOT:PSS (poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate))/SrTiO₃:Nb hybrid UV photodiode which is only activated in the UV region and exhibits a large response to the UV-B light. The studies on the organic/inorganic hybrid UV-A photodetectors are still not too much.

In this work, we have developed a UV-A hybrid detector based on a *p-n* junction consisting of *n*-type TiO₂ nanocrystals and *p*-type polymer PFH. The active hybrid layer of the device is prepared by spin-coating of the polymer solution mixed with ligand-capped TiO₂ nanocrystals. PFH has a large bandgap and strong absorption in UV-A range, which could be used as the donor and hole-

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transporting material. TiO₂ nanocrystals act as the acceptor and electron-transporting material. It has been found that high quality TiO₂ nanocrystals with good crystallinity and a narrow size distribution are very important for well-tailored chemico-physical properties [17]. And applications of the hybrids in the optoelectronic devices rely on the dispersion of the inorganic nanocrystals in the polymer matrix in order to create a high interfacial surface area for excitons diffusion to the interface and separation into free carriers [18,19]. In this work, the ligand (Oleic acid (OA)) used could fulfill all the requirements mentioned above. Furthermore, it is much cheaper compared with other commonly used ligands such as linoleic acid [20] and does not need a high reaction temperature to fabricate TiO₂ nanocrystals.

2. Experimental

2.1. Synthesis and characterization of monodispersed ligand-capped TiO₂ nanocrystals

Ligand-capped TiO₂ nanocrystals were synthesized using a solvothermal method. OA was used as the ligand. OA (63.5 mL), triethylamine (12.5 mL), NH₄HCO₃ (2.5 g), and cyclohexane (12.5 mL) were mixed at room temperature. Then 2.5 mL of Ti(OBu)₄ was added dropwise into the mixed solution. After stirring for 10 min, the solution was transferred into a 100 mL Teflon-lined autoclave and heated at 180 °C for 20 h. When cooled to room temperature, the crude product was precipitated with an excess of ethanol and washed with ethanol two times to remove the surfactant residuals. The final product was then dispersed in chloroform for further study.

X-ray diffraction measurement (XRD, RIGAKU D/MAX 2550/PC) with monochromatic Cu K α radiation was carried out to examine the crystal structure of the particles. The morphology was studied by transmission electron microscope (TEM, JEOL JEM-200 CX). Particle size was determined by a particle size analyzer (90Plus/BIMAS Multi Angle Particle Sizing Option, Brookhaven Instruments Corporation).

2.2. Fabrication and characterization of TiO₂ nanocrystals/PFH hybrids

In the preparation of hybrid films, the polymer PFH solution (2.5 mg/mL) was prepared by dissolving PFH (M_w = 24 000, PDI = 2.4, purchased from Beijing Synwit Technology Co. Ltd.) in chloroform. Hybrid dispersions with different contents of OA-capped TiO₂ nanocrystals were obtained by mixing the required amount of TiO₂ dispersion with PFH solution. Hybrid thin films were prepared by spin-coating the hybrid dispersion on the substrates for further use. The nanostructure was investigated by atomic force microscopy (AFM, Veeco Instruments Inc.) using tapping mode. Optical properties of the hybrid films were studied via UV–vis absorption measurements (Varian Cary100) and photoluminescence measurements (Perkin–Elmer LS55).

2.3. Device fabrication and characterization

The hybrid photosensitive layer (60 nm) made up of TiO₂ and PFH was spin-coated onto the PEDOT:PSS (40 nm) pre-coated ITO bottom electrode, followed by evaporation of a 40 nm thick Al electrode under vacuum. The effective cell area was adjusted to about 0.075 cm². The current–voltage (I–V) characteristic and photoresponse of the device were recorded with a Keithley 236 source-measure unit under the excitation of a high pressure mercury lamp (CHG-200) equipped with a 365 nm bandpass filter. For spectral response measurement, a 500 W Xenon lamp and a grating monochromator were used. The measurements were

conducted at room temperature in the air. To study the influence of annealing on the device performance, the as-prepared device was heated at 90 °C (the glass transition temperature of PFH is about 80 °C) in vacuum for variable duration.

3. Results and discussion

3.1. Morphology of monodispersed OA-capped TiO₂ nanocrystals and their hybrid films with PFH

Ligand-capped TiO₂ nanocrystals were synthesized at 180 °C using OA as the ligand. As shown in Fig. 1a, the typical peaks owing to the (101), (004), (200), (211), and (213) reflections of the anatase phase are found at $2\theta = 25.3, 37.8, 48.0, 54.0,$ and 62.7° , indicating that OA-capped TiO₂ nanocrystal powder is characteristic of bulk anatase TiO₂ with a high degree of crystallinity [21]. The particles' morphology is illustrated in the TEM image in Fig. 1b, from which the mean particle diameter is about 8–10 nm and no aggregates of TiO₂ nanocrystals are found with the help of the organic ligand [22]. The particle size distribution measured by a particle size analyzer was summarized in the inset of Fig. 1b. It is obvious that monodispersed nanocrystals have been obtained. The calculated average particle size is 10.5 nm, which is similar to that obtained from the TEM image.

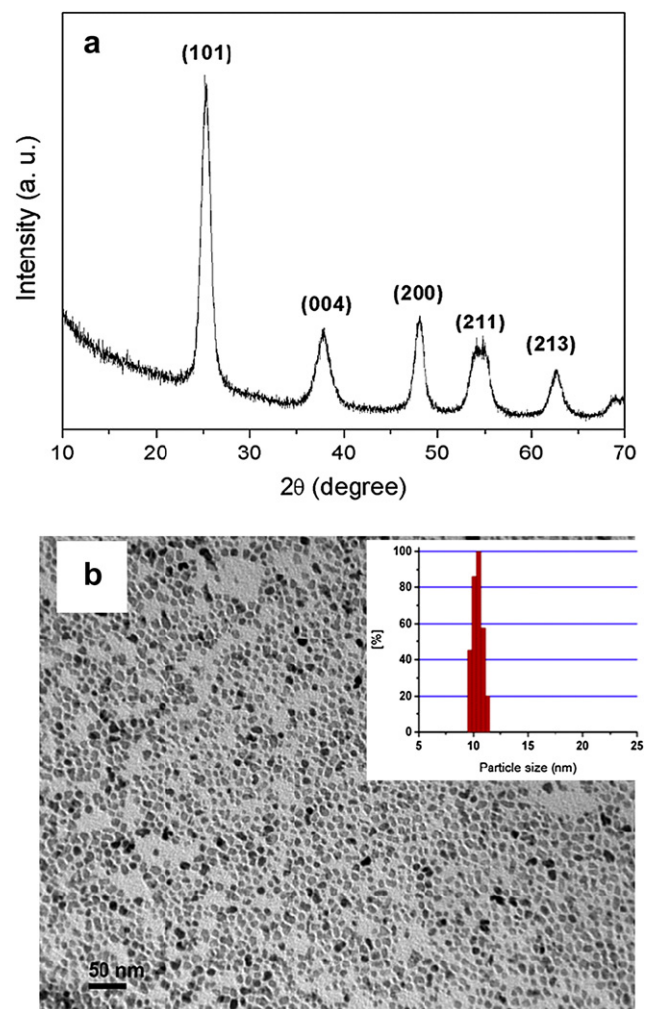


Fig. 1. XRD pattern (a) and TEM image (b) of the as-prepared OA-capped TiO₂ nanocrystals. The inset is the particle size distribution of the OA-capped TiO₂ nanocrystals.

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