



Effect of chemical structure of interface modifier of TiO₂ on photovoltaic properties of poly(3-hexylthiophene)/TiO₂ layered solar cells

Chih-Wei Hsu^a, Leeyih Wang^{a,b,*}, Wei-Fang Su^{a,c,*}

^a Institute of Polymer Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan

^b Center for Condensed Matter Sciences, National Taiwan University, Taipei, 10617, Taiwan

^c Department of Materials Science and Engineering, National Taiwan University, Taipei, 10617, Taiwan

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ABSTRACT

Two classes of phosphonic acid-bearing organic molecules, 2-oligothiophene phosphonic acid and ω -(2-thienyl)alkyl phosphonic acid were adopted as interface modifiers (IMs) of the TiO₂ surface, to increase its compatibility with poly(3-hexylthiophene) (P3HT). The self-assembled monolayers of these molecules on titania surface were characterized by making contact angle measurements and X-ray photoelectron spectroscopy (XPS). Atomic force microscopic (AFM) images revealed that the adsorption of IMs effectively smoothes the TiO₂ surface. Both photoluminescence (PL) spectroscopy and PL lifetime measurements were made to investigate the photoinduced properties of the TiO₂/IM/P3HT layered-junction. The PL quenching efficiency increased with the number of thiophene rings and as the alkyl chain-length in IMs decreased. Meanwhile, the decline in the PL lifetime followed a similar trend as the PL quenching efficiency. Additionally, the power conversion efficiency (PCE) of the ITO/TiO₂/IM/P3HT/Au devices was examined by measuring their photocurrent density–applied voltage (J – V) curves. The experimental results indicated that the short-circuit current density (J_{SC}) increased with the number of thiophene units and as the hydrocarbon chain-length in IMs decreased. However, the open-circuit voltage (V_{OC}) of the devices slightly fell as the energy level of the highest occupied molecular orbital (HOMO) of IM decreased. The PCE of the device with 2-terthiophene phosphonic acid was 2.5 times that of the device with 10-(2-thienyl)decyl phosphonic acid.

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1. Introduction

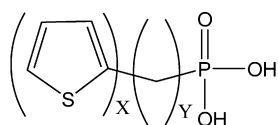
Traditional fuel energy resources are limited and generate harmful waste products in the atmosphere. Hence, alternative eco-friendly energy sources are receiving increasing attention. Of all substitute energy sources, solar power is most attractive because of its abundance and the consistency of sunlight. In 1950s, Chapin et al. at Bell laboratories developed the first crystalline silicon solar cell with a solar-energy conversion efficiency of 6% [1]. However, the relatively high cost of manufacturing these silicon cells has prevented them from extensive use. Moreover, another disadvantage of silicon cells is the use of toxic chemicals during manufacturing. Accordingly, the development of low-cost organic solar cells is urgent.

Conjugated polymer-based solar cells represent a growing area of research that holds promise for the creation of low-cost flexible devices for commercial application. In particular, polymer solar

cells offer numerous advantages in the area of fabrication, such as low cost, roll-to-roll production of large-area flexible solar cell. Given these advantages, the development of polymer solar cells is expected to have a major impact [2–6]. Polymer solar cells are usually fabricated from a photoactive layer which comprises an interpenetrating network of donor and acceptor materials [7,8]. This bulk-heterojunction structure has been widely studied and developed, because it can greatly increase the donor/acceptor interfacial area, promoting the dissociation of photogenerated excitons into charge carriers and enabling holes and electrons to be transported and collected. One of the most effective to date is the polymer/[6,6]-phenyl-C-61-butyric acid methyl ester (PCBM) blend system that has demonstrated a certified power conversion efficiency of around 5% [9]. Another promising approach is to use inorganic semiconductors as acceptors. In organic/inorganic bulk heterojunction photovoltaic cells, the active layer is constructed by blending conjugated polymer as donor with inorganic semiconductors as acceptor. This approach is gaining popularity because of its advantages: firstly, the hybrid material combines the advantages of high electron mobility, stability of inorganic materials and the solution-processing of polymers; secondly, the compensated light harvest of nanocrystals and conjugated polymers enlarges the ab-

* Corresponding authors at: Center for Condensed Matter Sciences, National Taiwan University, Taipei, 10617, Taiwan. Fax: +886 2 23696221.

E-mail addresses: leewang@ntu.edu.tw (L. Wang), suwf@ntu.edu.tw (W.-F. Su).



T1: X=1, Y=0
 T2: X=2, Y=0
 T3: X=3, Y=0
 N6: X=1, Y=6
 N10: X=1, Y=10

Fig. 1. The molecular structure of surface modifiers employed in this study.

sorption range, leading to the efficient conversion of sunlight [10]. In recent years, various solution-processed organic/inorganic bulk heterojunction photovoltaic cells have been reported. The inorganic particles used in those systems include CdSe [10–17], HgTe [18], TiO₂ [19–21] and ZnO [22–26] in nanosphere, nanorod or tetrapod shapes. However, when such a processing procedure has been employed, controlling the detailed morphology and dispersion of nanocrystals within the polymer has been difficult because of the incompatibility of organic polymer and inorganic semiconductor. Hence, the need for a surfactant that can control the dispersion of inorganic semiconductor nanocrystals in a wide variety of solvents and polymers is substantial [27]. In the case of CdSe and poly(2-methoxy-5-(2'-ethyl-hexyl-oxy)-*p*-phenylenevinylene) (MEH-PPV), a 1.1 nm-thick monolayer of the common surfactant, trioctylphosphine oxide (TOPO) is located on the surface of the CdSe nanocrystals, which disperse effectively in organic solvent, but sufficed to reduce electron transfer efficiency by a factor of ten [10]. W.J.E. Beek et al. used *n*-propylamine as surfactant to prepare a poly[2-methoxy-5-(3,7-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV)/ZnO bulk heterojunction. They showed that even though adding *n*-propylamine improved the film-forming properties of the blend, this addition still did not improve the performance of the photovoltaic cell [28]. Obviously, the choice of stabilizer or interface modifiers of nanocrystals is a key to improving the performance of a bulk heterojunction photovoltaic cell.

This work adopted two series of organic molecules with different chemical structures, 2-oligothiophene phosphonic acid with various thiophene rings (T-series) and ω -(2-thienyl)alkyl phosphonic acid with various alkyl chain lengths (N-series), as shown in Fig. 1, as interface modifier (IM), to investigate the structural effect of modifiers on the performance of organic/inorganic photovoltaic devices. A bilayer TiO₂/P3HT cell configuration was chosen for this study because the planar heterojunction between TiO₂ and P3HT not only eliminates complex issues concerning bulk heterojunctions such as pore filling, phase segregation and charge collection, but also ensures the optical interference profiles of devices are similar if the layers are of the same thicknesses [29,30]. Furthermore, results of studying a planar system may be directly applicable to bulk heterojunction systems.

2. Materials and methods

2.1. Synthesis of poly(3-hexylthiophene) and phosphonic acid-containing molecules as interface modifier

Phosphonic acid-containing molecules and regioregular poly(3-hexylthiophene) (P3HT) were synthesized via Grignard reaction method. The detailed synthesis and characterization procedures are provided in the Supplementary material.

2.2. Preparation of compact TiO₂ film

The ITO glass substrate (10 Ω /square) was cleaned with detergent followed by ultrasound cleaning for 15 min with deionized water, acetone and isopropyl alcohol and then drying in a vacuum oven at room temperature. A precursor solution of titanium isopropoxide-acetylacetonate complexes was prepared by mixing titanium isopropoxide (0.284 g) with acetylacetonate (0.2 g) in ethanol (30 ml). Precursor was deposited by the spray-pyrolysis method using N₂ as carrying gas at a flow rate of 7 L/min on a cleaned ITO glass surface preheated to 450 °C. After deposition, films were calcined under air for 5 min at 450 °C, which yielded flat TiO₂ films with a thickness of about 30 nm.

2.3. Preparation of self-assembled monolayers (SAMs) of phosphonic acid-containing molecules on compact TiO₂ film

SAMs were prepared by immersing TiO₂-coated ITO glass in an anhydrous tetrahydrofuran (THF) solution of 1 mM phosphonic acid-containing molecules for two days under ambient conditions. Substrates with SAMs were then rinsed with THF to remove residual reagents and then dried in a vacuum oven at room temperature.

2.4. Fabrication of photovoltaic devices

A chloroform solution of P3HT was spin-coated on the SAMs/TiO₂/ITO substrates. The thickness of the polymer layer was controlled by varying the spin speed and the concentration of the polymer solution. Au was then evaporated under vacuum (lower than 5×10^{-6} Torr) in an EDWARDS AUTO 306 vacuum evaporation system at 0.1 Å/s. The thickness of the gold was approximately 100 nm. The active area of each device was 4 mm \times 3 mm. Finally, the devices were annealed at 140 °C for 10 min in a glove box.

2.5. Characterization

The surface wettability of SAMs/TiO₂ substrates was studied by measuring the static contact angles with a First Ten Angstroms (FTA 125) contact angle analyzer at room temperature and ambient humidity, using water as the probe liquid. A 2 μ L water droplet was placed on the substrate *via* a syringe. The angle was obtained by estimating the tangent to the drop where it intersects the surface, and an average over five measurements was taken for reported contact angles. The X-ray photoelectron spectroscopic (XPS) analyses were conducted using a VG Scientific ESCALAB 250 system. Spectra were acquired at a base pressure of 10^{-9} Torr using a monochromatic AlK α X-ray source at 200 W. Samples were grounded to prevent charging, and charge compensation was applied. The survey scans were performed at an energy range of 0–1100 eV with a pass energy of 80 eV while core-level single spectra were collected using a pass energy of 20 eV and an acquisition time of 180 s. The binding energy was referenced to the C1s photoelectron peak of 284.6 eV.

Photoelectron spectroscopy in air (PESA) analyses were conducted using a Riken Keiki AC-2 UV photoelectron spectrometer. The UV source was 100 nW deuterium D₂ lamp with a spot diameter of 2 \times 2 mm. The samples were analyzed at 22 °C, 40% relative humidity and 1012 kPa pressure.

Atomic force microscopy (AFM) was performed in air using a Digital Instruments Nanoscope IIIa Multimode atomic force microscope in tapping mode. The nominal force constant of the silicon nitride cantilever (Nanoprobes Ltd.) was 0.12 Nm⁻¹. Cyclic voltammetry was carried out using a CHI 660 Electrochemical Analyzer with carbon, a Pt plate, and Ag/Ag⁺ electrode as the working,

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