Supplementary Data

Correlation between Nanoscale Surface Potential and Power Conversion Efficiency of P3HT/TiO_2 Nanorods Bulk Heterojunction Photovoltaic Devices

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The surface potentials of pristine P3HT films fabricated from different molecular weight

The three kinds of P3HT with low (10K Da), medium (30K Da), and high (66K Da) molecular weight are dissolved in chlorobenzene and then spin coated onto the indium-tin-oxide (ITO) glass. **Figure 1** shows topographic images **(a,c,e)** and surface potential mappings in dark **(b,d,f)** of pristine P3HT films fabricated from different molecular weights. The topography of three samples are very similar, and the average surface potentials are +415 mV **(Figure 1b)**, +394 mV **(Figure 1d)**, and

+393 mV **(Figure 1f)** for low, medium, and high molecular weight, respectively. The differences of surface potential are attributed to different degree of alignments and crystallinities of these P3HT. Moreover, the surface potential of these P3HT films with different molecular weight doesn't show obvious surface potential shift (<2 mV) between in dark and under illumination. The result implies no photoelectric phenomenon is present in pristine P3HT films.

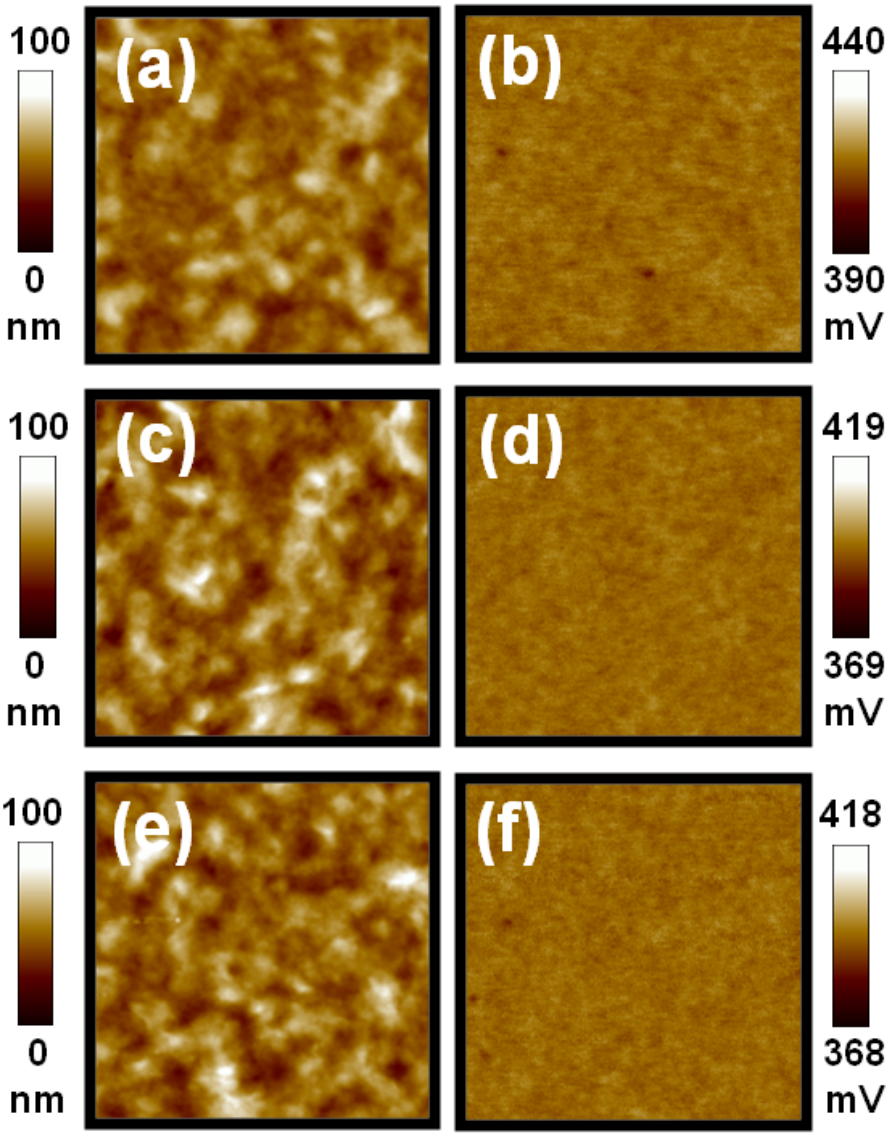

Figure 1 Topographic images **(a,c,e)** and surface potential mappings in dark **(b,d,f)** of pristine P3HT films made with low MW P3HT (**a,b**), medium MW P3HT (**c,d**) and high MW P3HT (**e,f**) on ITO glass substrate respectively. These image sizes are 5 × 5 μm.

The surface potentials of TiO_2 nanorods modified with different ligands

TiO_2 nanorods (NRs) modified with oleic acid, pyridine, oligomer 3HT-COOH are spin-coated from chloroform, pyridine, pyridine on the ITO glass substrate respectively. Figures 2a~e show topographic images and surface potential mappings of TiO_2 NRs modified with oleic acid (TiO_2-OA), TiO_2 NRs modified with pyridine (TiO_2-PYR), and TiO_2 NRs modified with oligomer 3HT-COOH (TiO_2-(3HT-COOH)) measured by KPFM. The average surface potentials are +76 mV for TiO_2-OA, +120 mV for TiO_2-PYR, and +150 mV for TiO_2-(3HT-COOH). The surface potential of TiO_2 nanorods modified with ligands is lower as compared with P3HT because the TiO_2 is an electron acceptor as oppose to the electron donor of P3HT. The more remnant free electrons in TiO_2 nanorods exhibits a low surface potential value. The surface potential of TiO_2-PYR (+120 mV) film is larger than that of TiO_2-OA (+76 mV) film because of the pyridine ligand is an electron donor as compared with charge neutral oleic acid ligand which results in hole accumulation on the surface. The surface potential of TiO_2-(3HT-COOH) film shows the largest value (+150 mV) due to its surface charges are dominated by hole accepting oligomeric 3HT segment of the ligand. The surface roughness of three films is in an increase order of TiO_2-(3HT-COOH)>TiO_2-PYR>TiO_2-OA which is due to a relative poor solvent of pyridine used in the first two films. Large aggregates formed in TiO_2-(3HT-COOH) film result in the largest surface roughness. When comparing the surface potential mappings for TiO_2 nanorods modified with different ligands, we found an interesting phenomenon. The surface potential shift between in dark and under illumination of TiO_2-OA film and TiO_2-PYR film are almost no change (<2 mV). However, TiO_2-(3HT-COOH) film shows a slight surface potential shift, about -5 mV, because the small amount of oligomer 3HT-COOH would absorb light and cause a photoelectric effect.

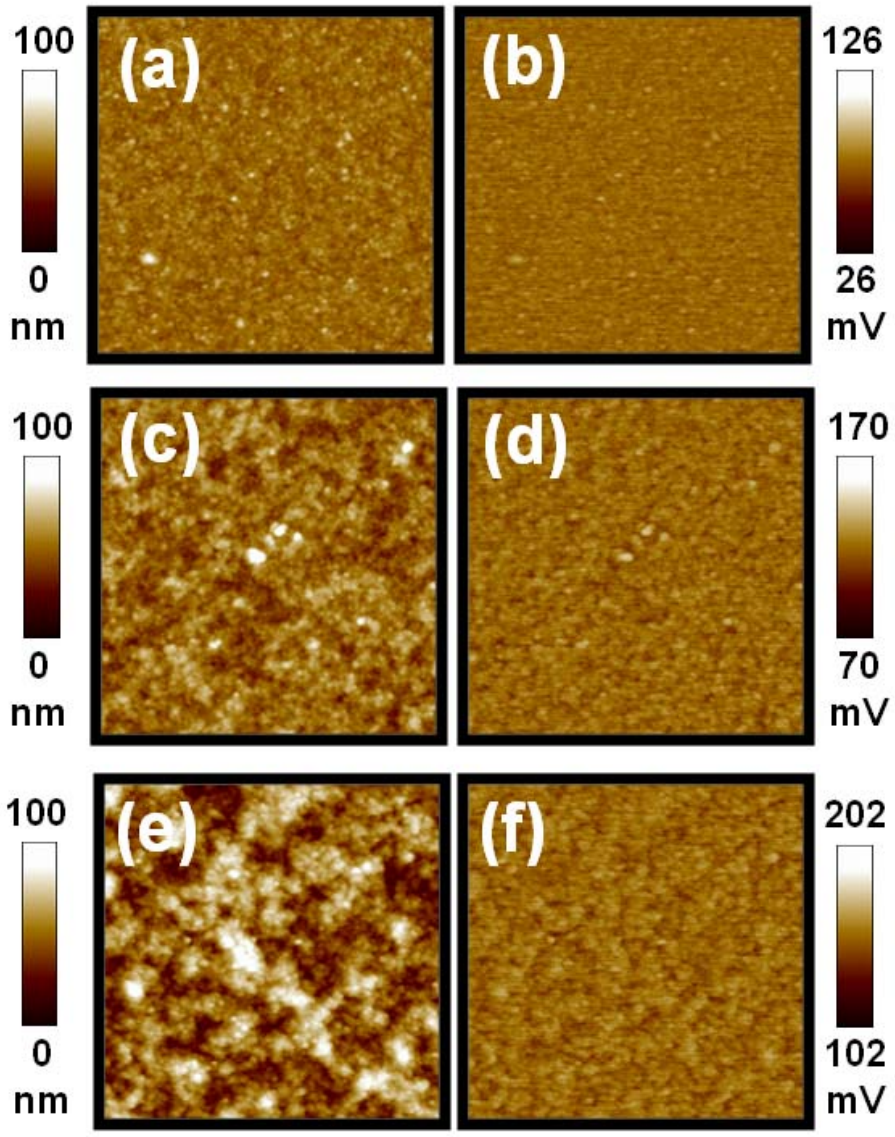

Figure 2 Topographic images **(a,c,e)** and surface potential mappings in dark **(b,d,f)** of the film made of TiO_2-OA (**a,b**), TiO_2-PYR (**c,d**) and TiO_2-(3HT-COOH) (**e,f**) on ITO glass substrate respectively. These image sizes are 5 × 5 μm.