Supporting Information

Local Photoelectric Conversion Properties of the Titanyl-phthalocyanine (TiOPc) Coated Aligned ZnO Nanorods

Liping Heng, [a] Dongliang Tian, [b] Long Chen, [c] Junxin Su, [b] Jin Zhai, * [a,b] Dong Han*[c] and Lei Jiang[a]

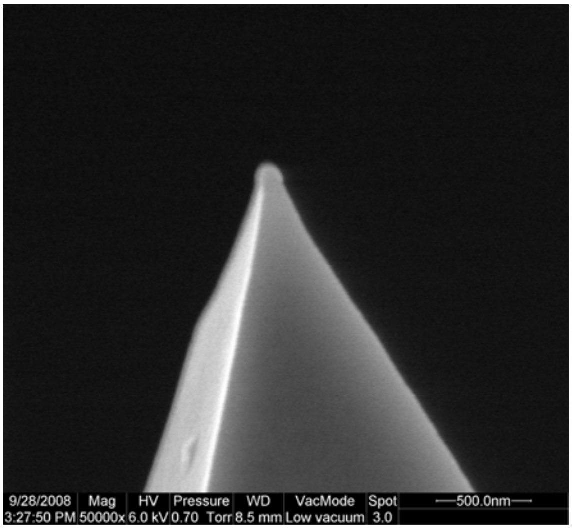


Fig. S1 The SEM image of the AFM tip, the diameter of the tip is about 60 nm.

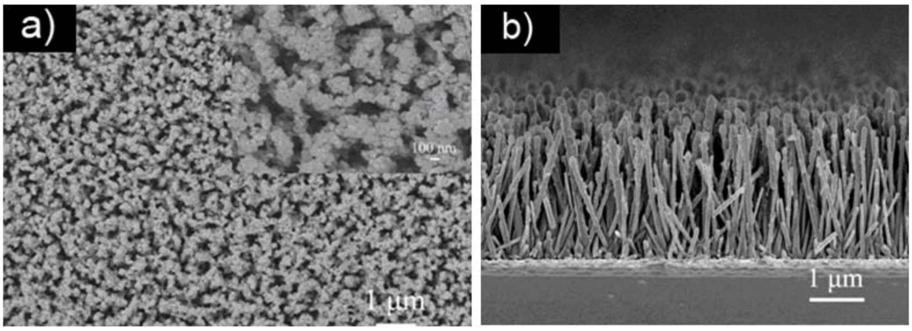


Fig. S2 (a) The typical field-emission scanning electron microscope (FE-SEM) top-images of the as-prepared films at low and high magnifications (inset); (b) The cross-section view of the sample, showing that the nanorods grow almost perpendicularly onto the substrates.

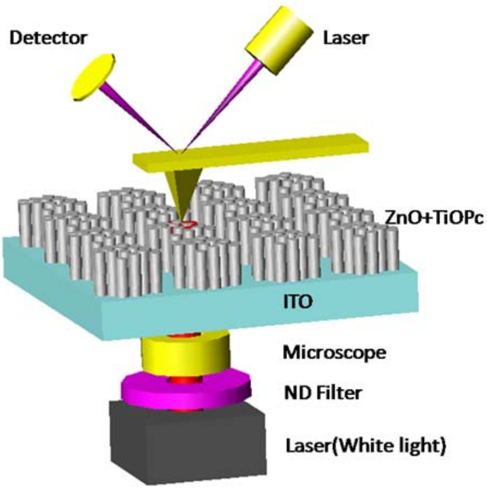
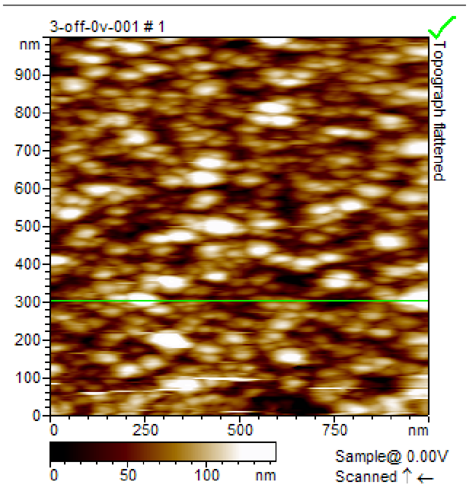
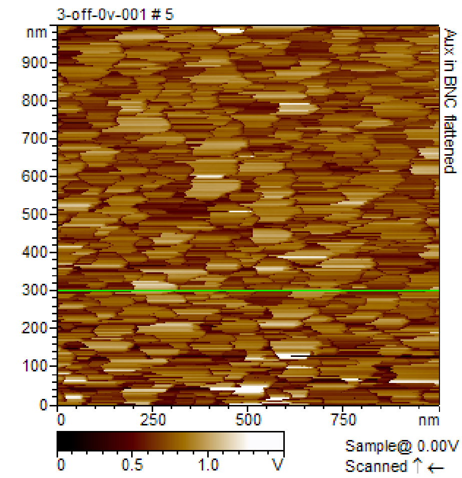


Fig. S3 Experimental schematic of a laser focused through a transparent electrode onto a photovoltaic film. Voltage and current are collected with a metal-coated AFM tip. This equipment is in the nitrogen atmosphere.

a)

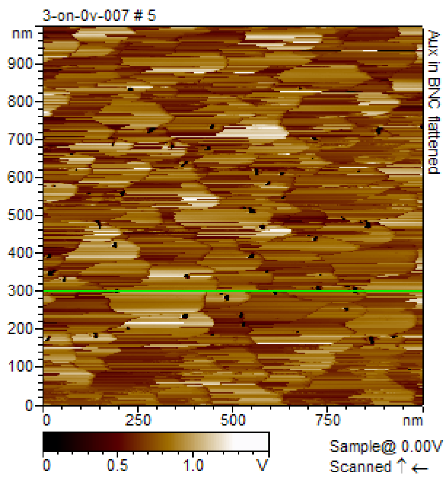


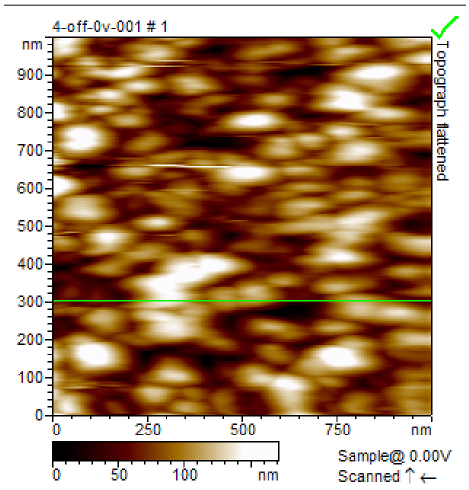
b)



c)

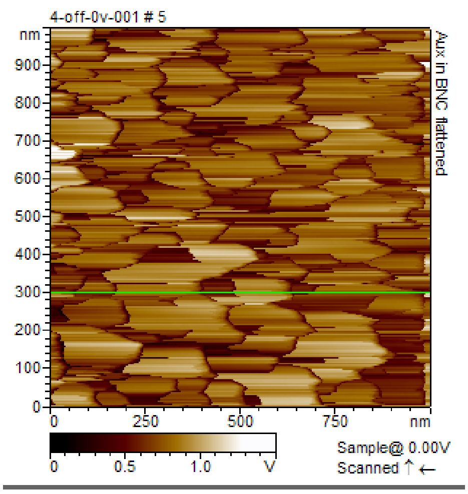
d)





e)

f)



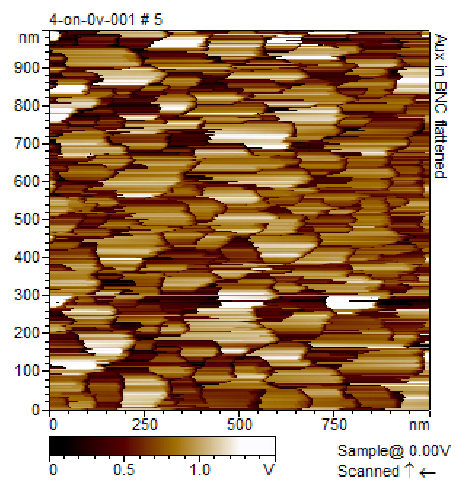


Fig. S4 AFM images of the aligned TiOPc/ZnO nanorods (100± 21 nm)film. (a) Topographic image; (b) Voltage image taken without the light irradiation; (c) Voltage image taken under the 30 mWcm^{-2} light irradiation. AFM images of the aligned TiOPc/ZnO nanorods (150± 18 nm) film. (d) Topographic image; (e) Voltage image taken without the light irradiation; (f) Voltage image taken under the 30 mWcm^{-2} light irradiation.

Explanation for Fig. S4: We chose different sets of nanowires with different diameters (for example about 60± 20nm, 100± 21 nm and 150± 18) to study the photovoltaic distributions in the micro-scale. As mentioned in this communication, the aligned ZnO nanorods were synthesized via a two-step solution method. By using this method, the diameter of the obtained nanowires is non-uniform and has distribution range. In Fig. S4 (a) shows the AFM height image of the aligned TiOPc/ZnO nanorods film. The bright regions correspond to the aligned TiOPc/ZnO nanorods, while the dim regions are the spaces between the TiOPc/ZnO nanorods. The diameter of the ZnO nanorod is non-uniform, and the diameter of the TiOPc/ZnO nanorods is 100±21 nm. Fig. S4 b) shows the voltage image collected from the TiOPc/ZnO aligned nanorods film without irradiation. It is measured in contact mode simultaneously with the height image. The bright domains suggest the charge accumulation to generate the ohmic contact voltage, which is caused by the contact potential difference between metal (tip coated with Pt) and semiconductor (TiOPc/ZnO). The irregular dim domains indicate the points where voltage is very low and no or little charge is generated. When a 30 $mWcm^{-2}$ white light irradiation attenuated by neutral density filters was focused onto the substrate and then aligned to the tip by using the inverted optical microscope, the photovoltage image in the micro-scale region was observed (Fig. S4 c)), and the photovoltage response during the scanning is stable. As shown, the bright regions on TiOPc/ZnO nanorods are becoming brighter than the ones in Fig. S4 b). This is due to the photoconductive properties of TiOPc/ZnO nanorods that provide charge accumulation on the surface by the light irradiation. For the TiOPc/ZnO nanorods with the diameter of 150±18 nm (Fig. S4 d), e), f)), there is a similar variation discipline. From Fig. S4c) and Fig. S4 f), it can be seen that the bright regions on TiOPc/ZnO nanorods (150±18 nm)are becoming brighter than the ones in Fig. S4 c). Therefore, the photovoltage increased with the increasing of the diameter of the nanorods, which is coincide with the conclusion we drawn in this manuscript.

Experimental Section:

Preparation: The aligned ZnO nanorods were synthesized via a two-step solution method. First, ZnO solution, prepared according to the method of Sakohara[1], was spun onto the ITO glass substrate three times and annealed at 420°C to prepare a 100 ~ 200 nm thick crystal seeds film. The as-prepared substrate was suspended in an aqueous solution of zinc nitrate hydrate (0.025 M) and methenamine (0.025 M) at 85°C for 15 h. Then it was removed from the solution, rinsed with deionized water and dried at 80°C for 10 h. TiOPc thin films were prepared by vacuum deposition method in a vacuum of 10^{-4} Pa onto the aligned ZnO nanorod array with the evaporation rate of ~ 0.06 nms^{-1}. The films of aligned TiOPc/ZnO nanorod array were obtained.

Characterization: Photoconductive-AFM was performed on the surface of aligned TiOPc/ZnO nanorods by an atomic force microscope (5500 Agilent Technologies Co.) in a nitrogen flow cell positioned above an inverted optical microscope. Figure S3 shows the experimental schematic. A conductive-AFM probe was aligned at the center of a diffraction-limited laser spot, which can generate enough photovoltage signals to facilitate imaging at modest voltage levels. The resolution of photovoltage image is 1 nA/V. The AFM's feedback diode has a wavelength of 670 nm, far outside the absorption profile of TiOPc or ZnO. Voltages were applied between the ITO substrate and the conductive probe tips, and the photovoltage was recorded by the currrent sensing nose. Platinum-coated, contact-mode AFM tips were used. The type is CSG10 and the tip aspect ratio is 3:1 – 7:1. The height and photovoltage were measured simultaneously in this case. The maximum z-scale for the voltage image of the instrument is 20 V. Morphology of the films was investigated using a JEOL JSM-6700F scanning electron microscopy (SEM) at 3.0 kV.

Notes and references

[1] S. Sakohara, L. D. Tickanen and M. A. Anderson, *J. Phys. Chem.* 1992, *96,* 11086.