Supporting Information

Enhancing photoresponsivity of self-powered UV photodetectors based on electrochemically reduced TiO_2 nanorods

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Experimental section

Growth of rutile TiO_2 nanorod arrays

The TiO_2 NRAs were grown on fluorine-doped tin oxide (FTO) glass by a hydrothermal method.[1] 0.1 mL tetrabutyl titanate (Alfa Aesar, 99%) was added dropwise into 10 mL HCl aqueous solution (6 M). Then the solution was transferred into a 30 mL Teflon-lined stainless autoclave with a piece of pre-cleaned FTO glass (ultrasonically cleaned with acetone, isopropanol, ethanol and deionized water for 20 min in sequence). The autoclave was then put into an oven and kept at 180 °C for 2 h and allowed to cool down to room temperature naturally. Finally, the sample was rinsed with copious deionized water and annealed at 450 °C for 2 h in a muffle furnace.

Electrochemical reduction of TiO_2 NRAs

The electrochemical reduction reaction was carried out in a conventional three-electrode system connected to a potentiostat (CHI 760D). The pristine NRAs electrode, a saturated calomel electrode (SCE) and a platinum plate were used as working, reference and counter electrodes, respectively. 0.5 M Na_2SO_4 aqueous solution (pH 6.8) was used as electrolyte. The external bias of −1.8 (*vs*. SCE) was applied and the obtained photoelectrodes are denoted as R-NRAs electrode.

Assembly of the UV detector

The pristine NRAs and the R-NRAs electrodes were directly used as photoanode of the detector. The counter electrode (CE) was platinized about 50 nm Pt over FTO pre-covered with 5 nm Tiby physical vapor deposition. The TiO_2 photoanode and the CE were separated by a hotmeltSurlyn film (60 μm thick) , and the redox electrolyte (0.1 M LiI, 0.05 M I_2, 0.6 M 1,2-dimethyl-3-n-propylimidazolium iodide, and 0.5 M 4-tert-butylpyridine in anhydrous acetonitrile) was injected into the interspace between the photoanode and CE.[2]

Sample characterization

The morphologies of rutile TiO_2 NRAs and R-NRAs were examined using a field emission scanning electron microscopy (SEM, Quanta 200 FEG, accelerating voltage

of 20 kV). High resolution transmission electron microscopy (HRTEM) images were obtained on a Tecnai G2 F30 S-Twin (FEI Company) with an acceleration voltage of 300 kV. The TiO_2 nanorod arrays were scraped off the FTO substrate and dispersed in water by ultrasonic, one drop of the aqueous suspension was then transferred onto a micrograte. The prepared samples were then dried in an oven at 60 ^oC overnight before TEM examination. UV−vis diffuse reflectance spectra (UV−vis) were recorded on a UV−vis spectrophotometer (JASCO V-550) equipped with an integrating sphere. Photocurrent measurements were conducted under irradiation by a 385 nm UV LED light with a CHI 760D to realize automatic data acquisition.The incident photon to current efficiency (IPCE) was evaluated under irradiation by a monochromatic tungsten lamp equipped with a monochromator (CROWNTECH, QEM24-D 1/4 m Double). The light intensity was calibrated with a standard Si photodiode. Mott−Schottky plots were evaluated with a three electrode system (electrolyte: 0.5 M Na_2SO_4) at DC potential range of −0.4~ 0.4 V *vs*. RHE at a frequency of 1 kHz in dark. Electrochemical impedance spectroscopy (EIS) was carried out at certainopen circuit potentials, with an AC potential frequency ranging from 100K to 0.1 Hz under 385 nm UV LED (4 mW cm^{-2}) irradiation. The program ZView (Scribner Associates Inc.) was used to fit the obtained data to the corresponding equivalent circuit model.

Figures

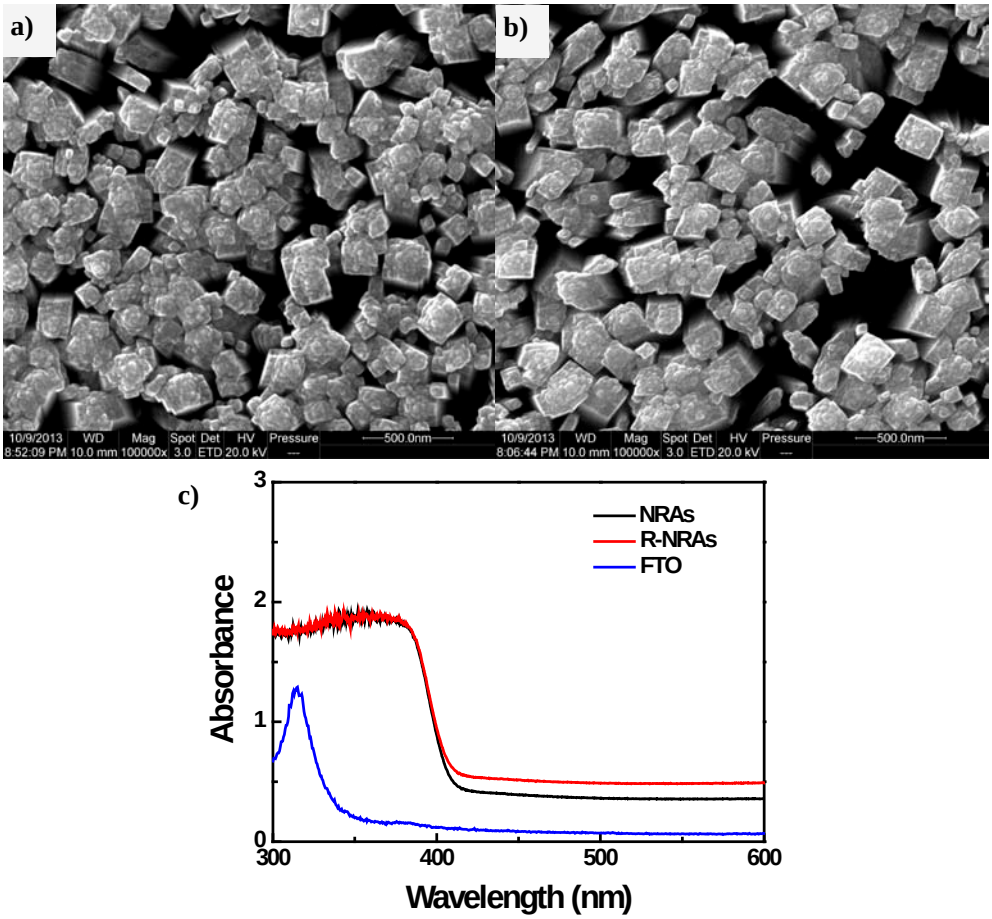

Figure S1. SEM top−view images of (a) NRAs and (b) R−NRAs. (c) UV−vis Spectra of NRAs, R−NRAs and FTO substrate.

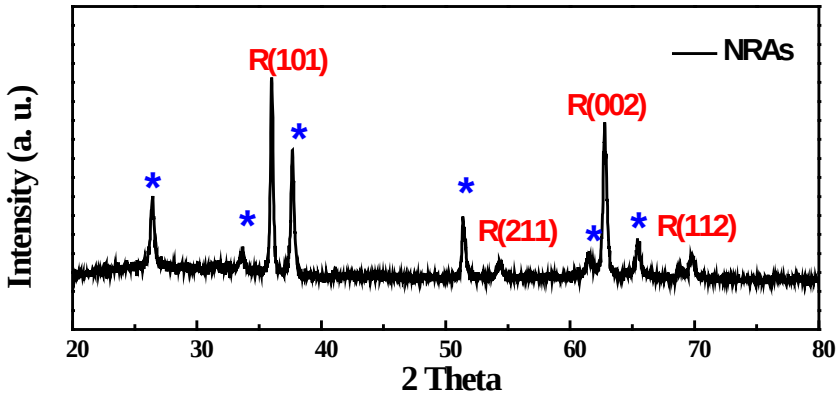

Figure S2. XRD patterns of the NRAs, peaks marked with (*) are the diffraction peaks of the FTO substrate.

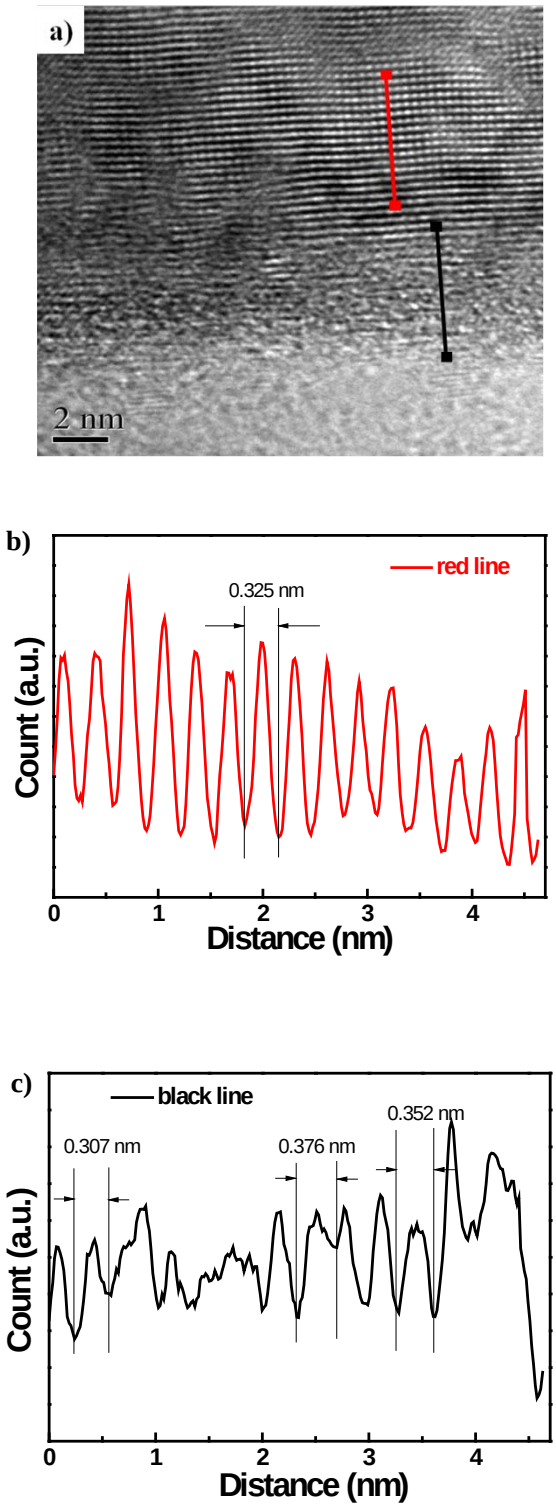

Figure S3. (a) HRTEM images of R-NRAs, (b) red line and (c) black line analyses of R-NRAs.

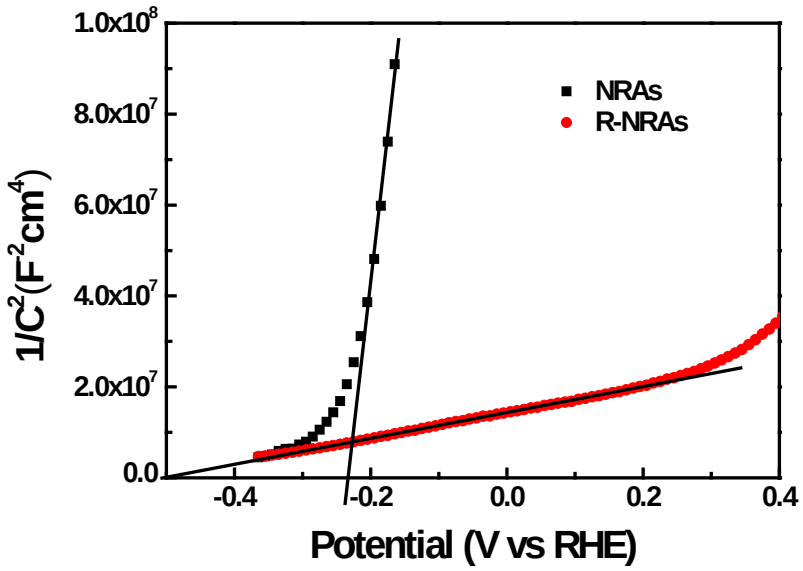

Figure S4. Mott−Schottky plots of NRAs and R−NRAs.

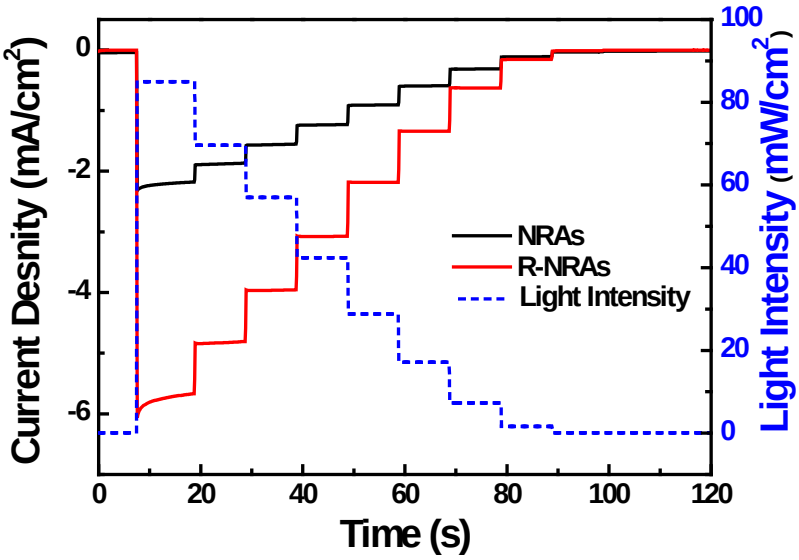

Figure S5. The light density dependent photocurrent response of the NRAs and R−NRAs devices (light wavelength: 385 nm).

Reference

1. P. Yan, G. Liu, C. Ding, H. Han, J. Shi, Y. Gan and C. Li, *ACS Appl. Mater. Interface*, 2015, **7**, 3791-3796.
2. X. Zheng, J. Deng, N. Wang, D. Deng, W.-H. Zhang, X. Bao and C. Li, *Angew. Chem.-Int. Edit.*, 2014, **53**, 7023-7027.