

Electronic Supplementary Information (ESI)

**Thermal Vacuum De-oxygen and Post Oxidation of TiO₂ Nanorod
Arrays for Enhanced Potoelectrochemical Properties**

Chao Huang,^{a,b,‡} Juncao Bian,^{a,b,‡} Yao Guo,^{a,b} Miaoyan Huang,^{a,b} Rui-Qin Zhang^{a,b,c}*

^a Department of Physics, City University of Hong Kong, Hong Kong SAR, China

^b Shenzhen Research Institute, City University of Hong Kong, Shenzhen, China

^c Beijing Computational Science Research Center, Beijing 100193, China

[‡] These authors contribute equally to this work.

* Corresponding author; E-mail: aprqz@cityu.edu.hk

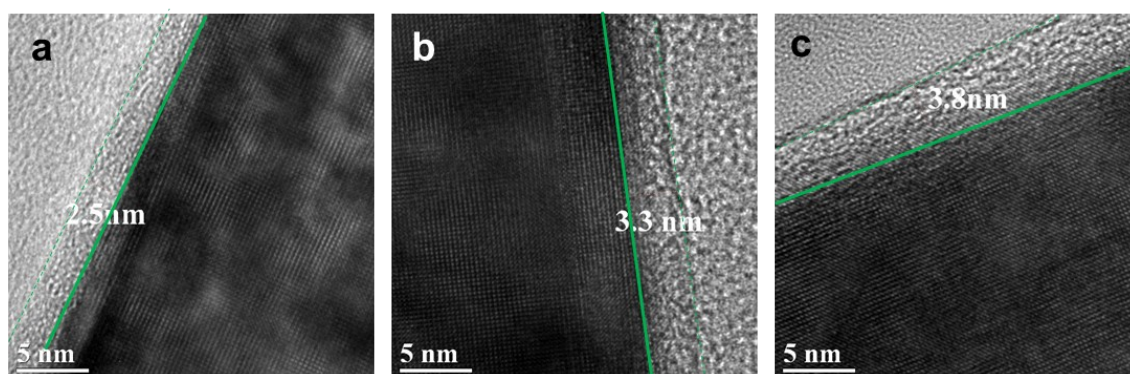


Fig. S1 SEM images of TiO_{2-x} -15, TiO_{2-x} -30, and TiO_{2-x} -60 NRAs.

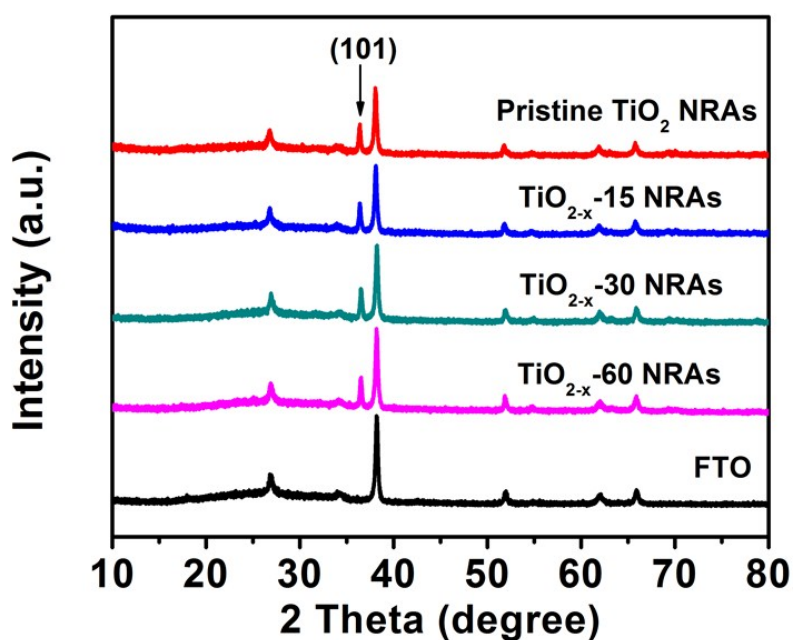


Fig. S2 XRD patterns of FTO, pristine TiO_2 NRAs, and TiO_{2-x} -15, TiO_{2-x} -30, and TiO_{2-x} -60 NRAs.

Fig. S2 displays the XRD patterns of the pristine TiO_2 NRAs, TiO_{2-x} -15, TiO_{2-x} -30, TiO_{2-x} -60 NRAs, and bare FTO, respectively. Comparing with FTO, one more peak can be found at the two theta degree of 36.1, attributing to the (101) plane of rutile TiO_2 (JCPDS No.21-1276). As it can be seen, no obvious phase transformation occurred after the thermal treatment in vacuum.

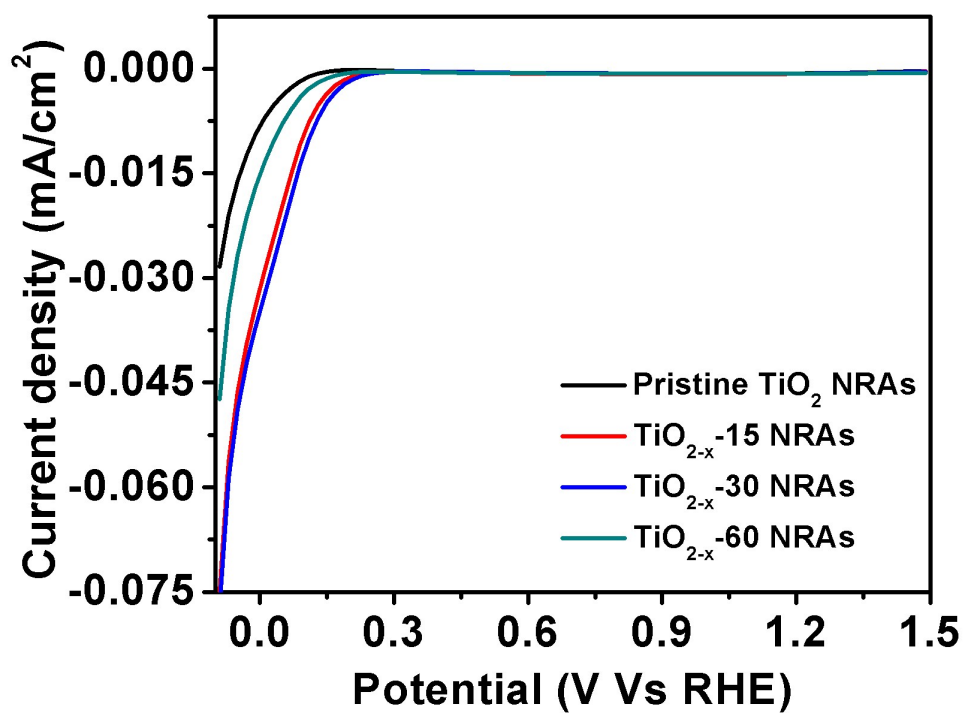


Fig. S3 LSV curves of pristine TiO₂ NRAs, and TiO_{2-x}-15, TiO_{2-x}-30, and TiO_{2-x}-60 NRAs. (without light illumination)

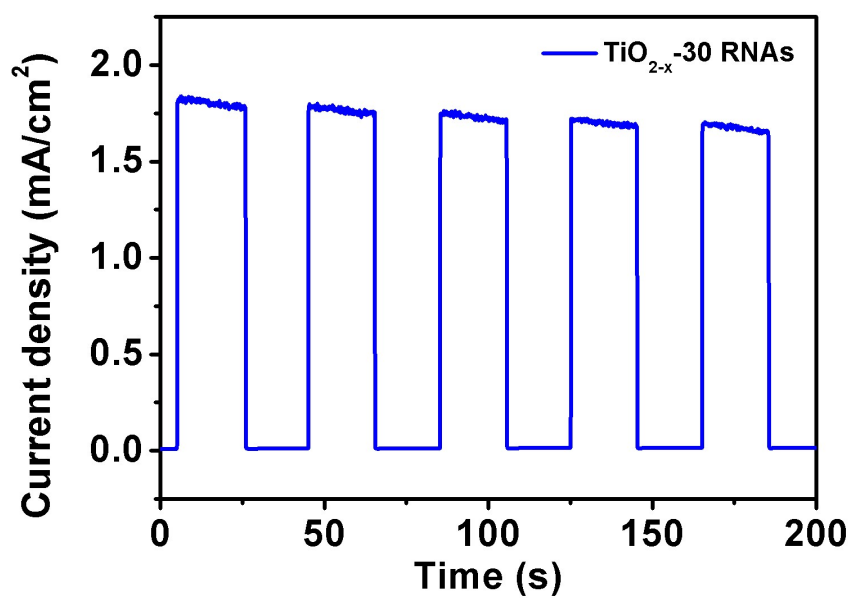


Fig. S4 Photocurrent response measured in Na₂SO₄ electrolyte with Na₂S as sacrificial reagent.

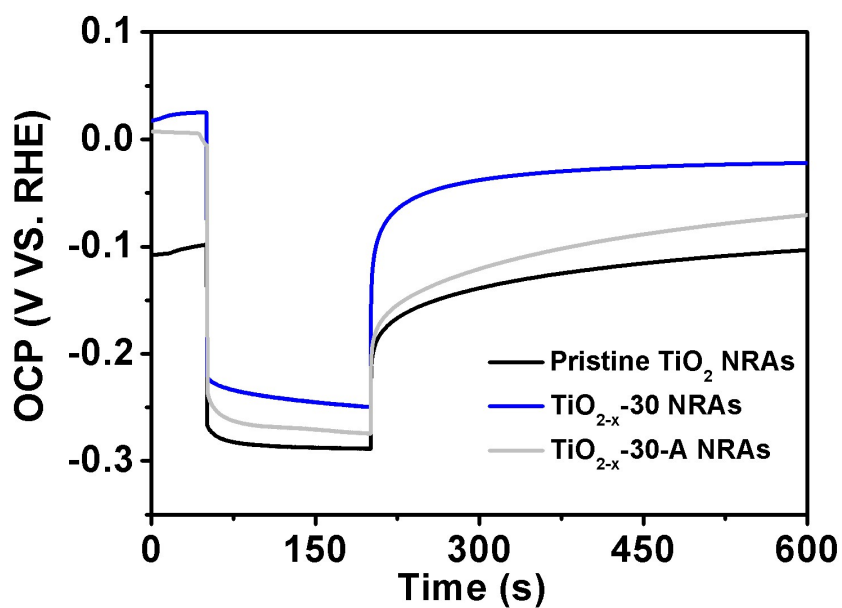


Fig. S5 Open circuit potential of pristine, TiO_{2-x}-30 and TiO_{2-x}-30-A NRAs.

The photovoltage of modified electrode (TiO_{2-x}-30-A) is larger than that of pristine TiO₂ NRAs. Fig. S5 displays the open-circuit potential of both pristine TiO₂, TiO_{2-x}-30 and TiO_{2-x}-30-A NRAs in the dark and light. The difference between the potentials that obtained from the dark and light situations led to the photovoltage. The measured photovoltage of pristine TiO₂ NRAs is 0.18 V, and significantly higher values of 0.21 and 0.26 V are obtained from TiO_{2-x}-30 and TiO_{2-x}-30-A NRAs, respectively. The improvement of photovoltage is attributed to the enlarged band bending of TiO_{2-x}-30-A NRAs after oxygen vacancy generation.