Electronic Supplementary Material (ESI) for Nanoscale.

Supporting Information for

Cobalt phosphate modified TiO_2 nanowire arrays as co-catalyst for solar water splitting

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Experimental section

Preparation of TiO_2 nanowire arrays

TiO_2 nanowire arrays were grown onto fluorine-doped tin oxide (FTO) glass substrates using a hydrothermal method reported elsewhere with minor modification.[1] Briefly, 0.3 ml titanium n-butoxide and 0.6 g NaCl were added into the 25 ml diluted hydrochloric acid (mass fraction 18.25-19%) and stirred until the mixture became clear. After that, the above precursor was transferred into a 100 ml Teflon-lined stainless steel autoclave in which the FTO substrates were placed with an angle against the in-wall with the conductive side facing down. The hydrothermal process was conducted in an electric oven at 150 ℃ for 10 h. After cooling, the resultant samples were removed and rinsed with water to get rid of any residual reactants and dried in air at 80 °C. Finally, the as-grown TiO_2 nanowire arrays were annealed at 550 °C for 2 h in air to improve the crystallinity.

Photo-electrodeposite Co-Pi catalyst onto TiO_2 nanowire array

The Co-Pi catalyst was deposited onto TiO_2 nanowrie array by photo-assisted electrodeposition in 0.1 M potassium phosphate buffer electrolyte containing 0.5 mM cobalt nitrate under AM 1.5 simulated backside solar irradiation (through the FTO). The amperometric i-t curve technique was used for Co-Pi depositions near the open circuit potential with a supercritical positive current applied (a typical deposition curve was shown in Fig. S1). This deposition process provides an efficient way to couple the oxygen evolution catalyst with photoanode by naturally placing the catalyst at the location where the holes are most readily available for O_2 evolution.

The amount of Co-Pi was controlled by varying the quantity of electric charge passed through the external circuit. A relative thick Co-Pi (10 mC cm^{-2}) was deposited on the TiO_2 nanowire arrays for as samples for XRD and UV-vis measurements. After deposition, the electrode was washed with DI water to remove any residual electrolyte.

Structural and optical characterizations

The morphology and microstructure of the samples were characterized using the field emission scanning electron microscope (NOVA NANOSEM 450, FEI, USA) equipped with an energy-dispersive X-ray spectroscopy (EDS). The crystal structures were characterized by a Rigaku Dmax 2500 X-ray diffractometer with Cu K_α radiation. The surface composition and elemental chemical state of the samples were examined by X-ray photoelectron spectroscopy (XPS) using a K-Alpha 1063 (Thermo Fisher Scientific, UK) equipped with Al Ka monochromator X-ray source. The light absorption was recorded by UV-vis spectrophotometer (UV-2500, Shimadzu, Japan).

Photoelectrochemical measurements

The PEC performance of the electrodes were studied on three-electrode system using electrochemical workstation (CH Instruments, model CHI660E). The modefied TiO_2 or pristine TiO_2 NWAs on FTO substrates were used as the working electrodes, a Pt foil as counter electrode and Ag/AgCl as reference electrode. Unless otherwise stated, the 0.1 M potassium phosphate (ph=7) was used as electrolyte for all PEC measurements. The photocurrent densities were measured under AM 1.5 simulated sunlight back side illumination using a 150 W Xe lamp. The incident light intensity was monitored to 100 mW cm^{-2} all through the measurement period using a digital power meter. Mott−Schottky plots were measured in the dark at an AC frequency of 5 and 10 kHz. Another four equal 0.1 M potassium phosphate (ph=7) electrolyte were prepared and the pH value of which were precisely adjusted to 1, 4, 10 and 14 respectively using concentrated KOH or H_2SO_4 electrolyte, for photocurrent-potential curves test in different pH condition. Hereafter, the electrode potential versus the Ag/AgCl is converted to the reversible hydrogen electrode (RHE) potential according to the Nernst equation[2]: $E_{RHE} = E_{Ag/AgCl} + 0.059pH + E^{\theta}_{Ag/AgCl}$, where E_{RHE} is the converted potential *vs.* RHE, $E^{\theta}_{Ag/AgCl}$ = 0.1976 V at 25 °C, and $E_{Ag/AgCl}$ is the experimental potential measured against the Ag/AgCl reference electrode.

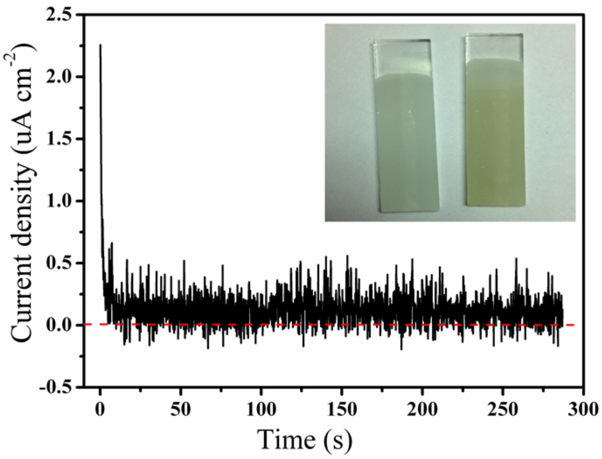

Fig. S1. Typical *i-t* curve recorded during the photo-electrodeposition process. The inset is the corresponding photograph of the pristine TiO_2 electrode (left) and TiO_2/Co-Pi (10 mC cm^{-2}, right) composite electrode.

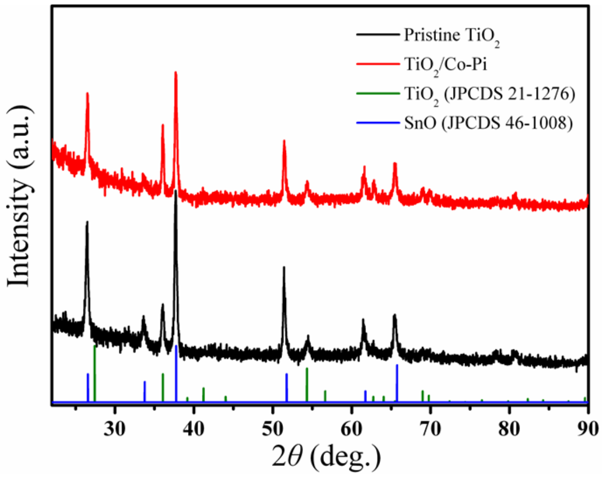

Fig. S2. XRD spectra of the pristine TiO_2 and TiO_2/Co-Pi nanowire array photoelectrodes.

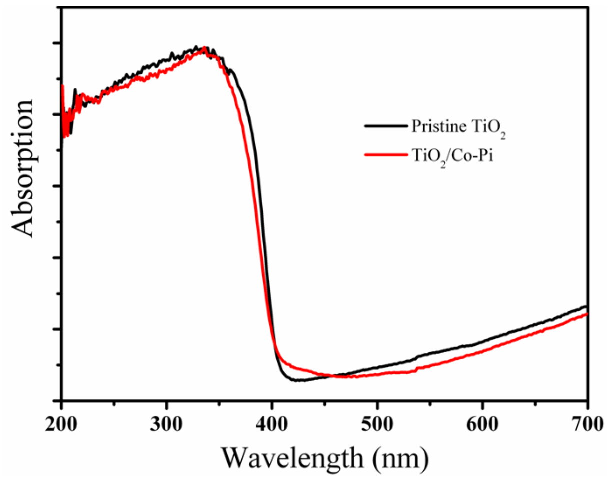

Fig. S3. UV-vis spectra of the pristine TiO_2 electrode and TiO_2/Co-Pi (10 mC cm^{-2}) composite electrode.

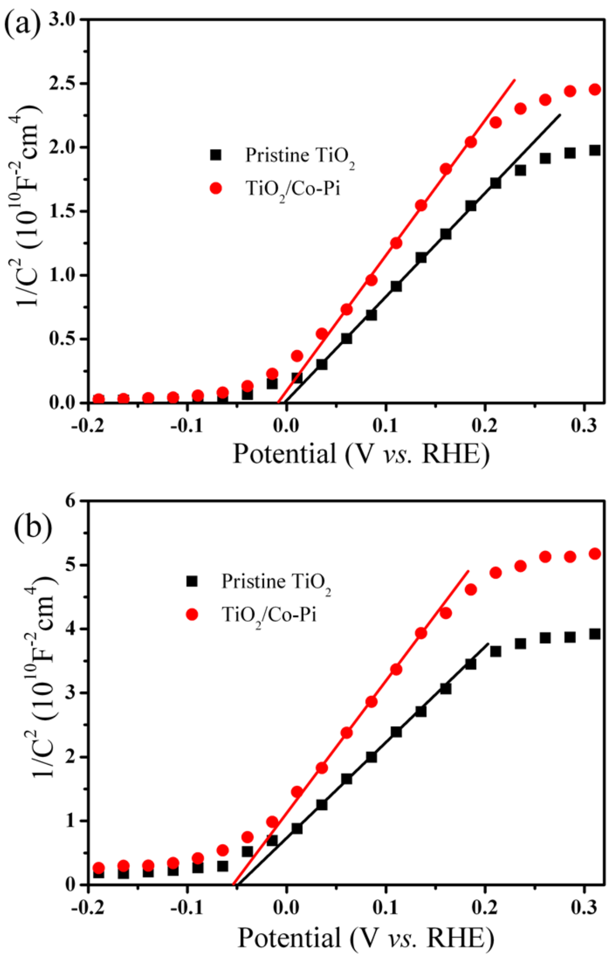

Fig. S4. Mott-Schottky plots of the pristine TiO_2 electrode and TiO_2/Co-Pi composite electrode collected at frequency of (a) 5 kHz and (b) 10 kHz under dark in 0.1 M potassium phosphate electrolyte (pH=7). The flat band potentials of the TiO_2/Co-Pi and pristine TiO_2 nanowire arrays are determined by extrapolating the X-intercepts of the linear region in these plots. It can be seen that the pristine TiO_2 and composite TiO_2/Co-Pi electrodes have comparable flat band potentials under a certain frequency, i.e., both 0 V *vs.* RHE at frequency of 5 kHz and -0.05 V *vs.* RHE at frequency of 10 kHz.

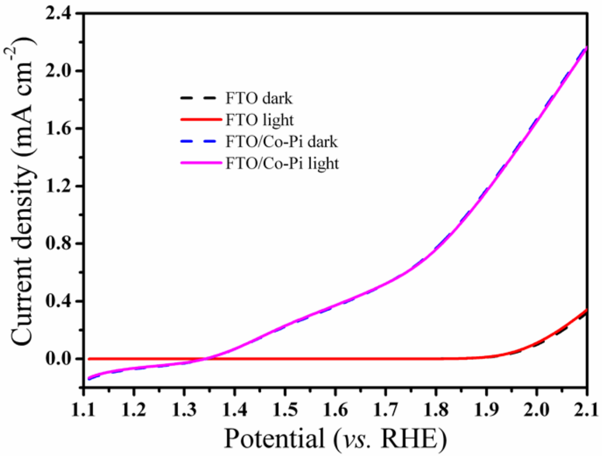

Fig. S5. Linear sweep voltammograms collected for FTO substrate with and without Co-Pi catalyst in the dark (dashed line) and under 1 sun illumination (solid line) in 0.1 M potassium phosphate electrolyte (pH=7). The overlapped i-v curves under light and dark of FTO/Co-Pi or FTO demonstrate that there is no photocurrent originated from the Co-Pi or FTO substrate.

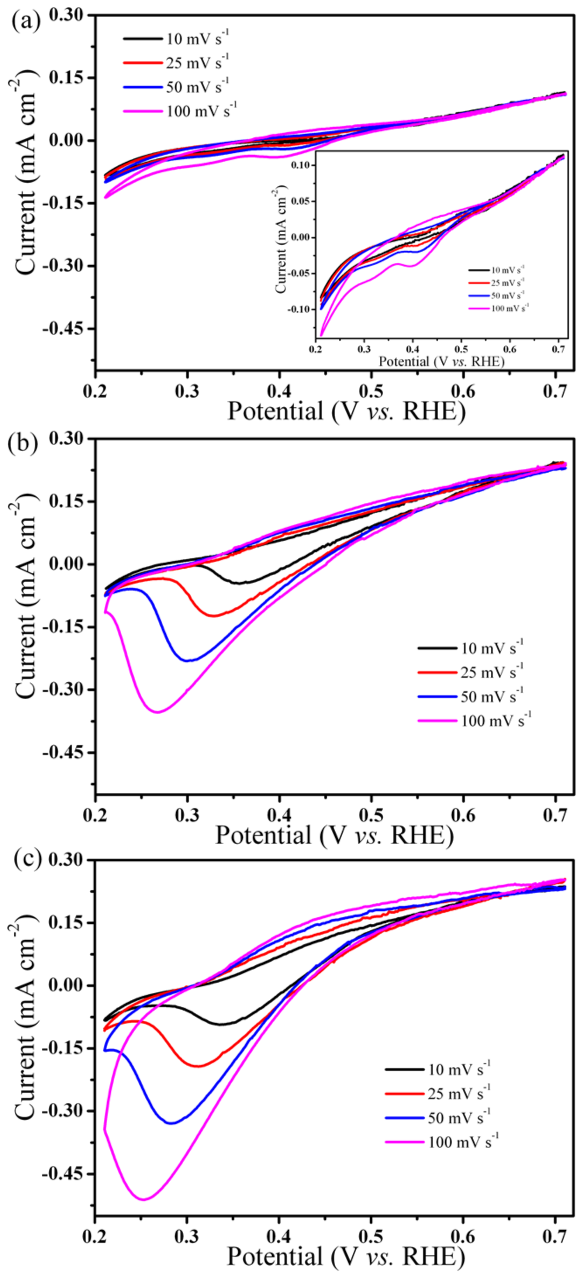

Fig. S6. Cyclic voltammograms of (a) pristine TiO_2 with its magnified graph inserted, (b) TiO_2/Co-Pi with 10 uC cm^{-2} and, (c) and TiO_2/Co-Pi with 1 mC cm^{-2} deposition in 0.1 M potassium phosphate electrolyte (pH=7) at different scan rate under 100 mW cm^{-2} illumination.

References:

1. G. Ai, R. Mo, H. Xu, Q. Chen, S. Yang, H. Li and J. Zhong, *J. Appl. Phys.*, 2014, 116, 174306.

2. M. Gratzel, *Nature*, 2001, 414, 338-344.