Electronic Supplementary Material (ESI) for Dalton Transactions.

Ni_2P modified Ti^{4+} doped Fe_2O_3 photoanode for efficient solar water oxidation by promoting hole injection

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EXPERIMENTAL SECTION

1. Preparation of Samples

Preparation of Ti-Fe_2O_3 photoanodes: Ti-Fe_2O_3 photoanodes were fabricated according to our previous report.[1] Typically, 1 mL 0.05% (volume percentage) $TiCl_4$ (99%, Sinoreagent Co., Ltd) ethanol solution was added in 30 ml aqueous solution containing 0.15M $FeCl_3\cdot6H_2O$ (99%, Aladdin) and 1M $NaNO_3$ (99%, Sinoreagent Co., Ltd). The mixed solution was transferred to a teflon-lined autoclave. A fluorine-doped tin oxide glass (FTO, Nippon Sheet Glass) of 1 × 2.5 cm was cleaned with deionized water, ethanol, acetone, ethyl acetate and placed in the teflon-liner. The teflon-lined autoclave was sealed and maintained at 100 ºC for 12 h. Finally, the obtained Ti-Fe_2O_3 film was thoroughly washed by deionized water and annealed in air at 550 ºC for 2 h.

Preparation of Ni_2P nanoparticles: Ni_2P nanoparticles were synthesized according to our previous report.[2]

Preparation of Ti-Fe_2O_3/Ni_2P photoanodes: A drop-casting technique was used to synthesize the Ti-Fe_2O_3/Ni_2P photoanodes.[3] Firstly, 2 mg of Ni_2P nano-particles were dispersed in 10 mL absolute ethanol and sonicated for 15 min to form a uniform nanoparticle "ink". The "ink" was then drop-casted into the Ti-Fe_2O_3 photoanodes. The drop-casted area was controlled to be 2.5 cm^2 and the mass of the Ni_2P was adjusted by the drop volume of "ink". The composites were fully dried at 80 °C for 1 h. In order to investigate the effects of Ni_2P loading on the photocatalytic activity, the Ti-Fe_2O_3/Ni_2P photoanodes with various drop volume (100μL, 200μL, 400μL) were prepared (respectively denoted as Ti-Fe_2O_3/Ni_2P100, Ti-Fe_2O_3/Ni_2P200, Ti-Fe_2O_3/Ni_2P400).

Note: If not specially indicated, the Ti-Fe_2O_3/Ni_2P represent Ti-Fe_2O_3/Ni_2P200 in the manuscript and supporting information

2. Characterization

Gemini 550 field-emission scanning electron microscope (Zeiss Company) and JEM-2010 transmission electron microscope (JEOL Ltd.) were used to characterize the morphologies of the samples. The crystal structure of the as-prepared samples was characterized by X-ray diffraction (XRD) using a Rigaku D/Max-2550 X-ray diffractometer with Cu–Kα radiation ($\lambda = 1.5418$ Å) at 50 kV and 200 mA in the 2θ range of 20–80° with a scanning rate of 5° min^{-1}. The optical absorption spectra of the samples were measured using a UV-vis-NIR spectrophotometer (Shimadzu UV-3600) over the range of 300–800 nm. The lock-in amplifier-based SPV measurement was carried out on home-made systems, which has been described previously.[4] Typically, SPV measurement system is constituted of a 500 W xenon lamp (LSH-X500, Zolix), a grating monochromator (Omni-5007, Zolix), a lock-in amplifier (SR830-DSP, Stanford) with a light chopper (SR540, Stanford), a photovoltaic cell and a computer. A low chopping frequency of 23 Hz was used in the conventional testing. XPS measurements were performed on a Thermo VG Scientific ESCALAB 250 spectrometer with monochromatized $\text{Al}_{\text{K}\alpha}$ excitation.

Current density vs. applied potential (*J–V*) curves were measured with an electrochemical analyzer (LK2006A, Lanlike) using Ag/AgCl as the reference electrode and a Pt wire as the counter electrode. The applied potential used in this paper was converted to be versus the reversible hydrogen electrode (RHE) using the Nernst equation:

$$E_{RHE} = E_{Ag/Agcl} + 0.0591 \times pH + 0.1976V$$

An aqueous solution of 1 M KOH was used as the electrolyte (pH = 13.6). The light source was provided by a 300 W xenon lamp (PLS-SXE300, trusttech), and the white light intensity was adjusted to 100 mW cm^{-2}.

For incident-photon-to-current efficiency (IPCE) measurements, monochromatic light was provided by light emission from a 300 W xenon lamp (PLS-SXE300, trusttech) passing through a grating monochromator (Omni-5007, Zolix). The intensity of the monochromated light was measured using an irradiatometer (FZ-A, Photoelectric Instrument Factory of Beijing Normal University). The IPCE values were calculated using the following equation:

$$IPCE = \frac{J \times 1240}{P_{mono}\,\lambda}$$

where J is the photocurrent density (mA cm^{-2}), P_{mono} is the light power intensity (mW cm^{-2}) of the monochromatic light, and λ is the wavelength of incident light (nm).

To examine the injection efficiency (η_{inj}), 0.5 M H_2O_2 was added to the electrolyte solution because the oxidation of H_2O_2 is thermodynamically and kinetically more favorable than water. When the photocurrent is recorded in the KOH/H_2O_2 electrolyte, it is believed that PEC performance of the electrode is independent of the kinetic of the surface reaction. The injection efficiency (η_{inj}) were calculated using the following equation:

$$\eta_{inj} = J_{PEC} \,/\, J_{H_2O_2}$$

where J_{PEC} is the water splitting photocurrent, $J_{H_2O_2}$ photocurrent obtained in KOH/H_2O_2 electrolyte.

The Nyquist plots calculated from electrochemical impedance spectroscopy (EIS) were performed from 100 000 to 0.05 Hz under illumination.

The Mott–Schottky calculations derived from impedance measurements in the dark at 1000 Hz. The donor concentration (N_d) and flat band potential (V_{fb}) can be quantified by the Mott-Schottky equation:

$$1/C^2 = (2/e\varepsilon_0\varepsilon N_d)\left[(V - V_{fb}) - KT/e\right]$$

Where the C is the capacitance of the space charge region, ε_0 is the vacuum permittivity, ε is the dielectric constant of α-Fe_2O_3, e is the electron charge, V is the electrode applied potential, K is the Boltzmann constant, T is the absolute temperature, and N_d is the donor concentration. The donor concentration is calculated with the equation:

$$N_d = (2/e\varepsilon_0\varepsilon)\left[d(1/C^2)/dV\right]^{-1}$$

Accumulated charge density measurements were obtained by integration of the initial current spike.

ADDITIONAL FIGURES

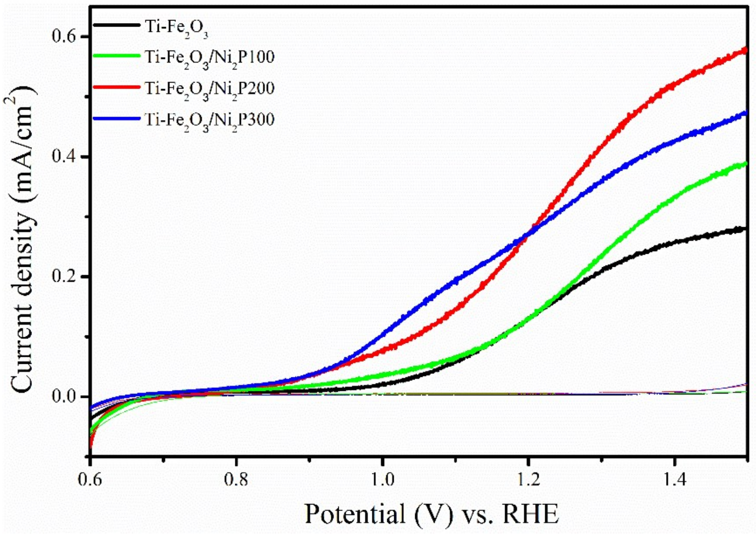

Figure S1. Photocurrent and dark current densities of Ti-Fe_2O_3, Ti-Fe_2O_3/Ni_2P100, Ti-Fe_2O_3/Ni_2P200 and Ti-Fe_2O_3/Ni_2P400 electrodes under 100 mW/cm^2 xenon light illumination in 1 M KOH electrolyte.

The Ti-Fe_2O_3/Ni_2P200 electrode exhibited the best PEC water oxidation performance. Therefore, we select this electrode as the object to discuss in the main manuscript.

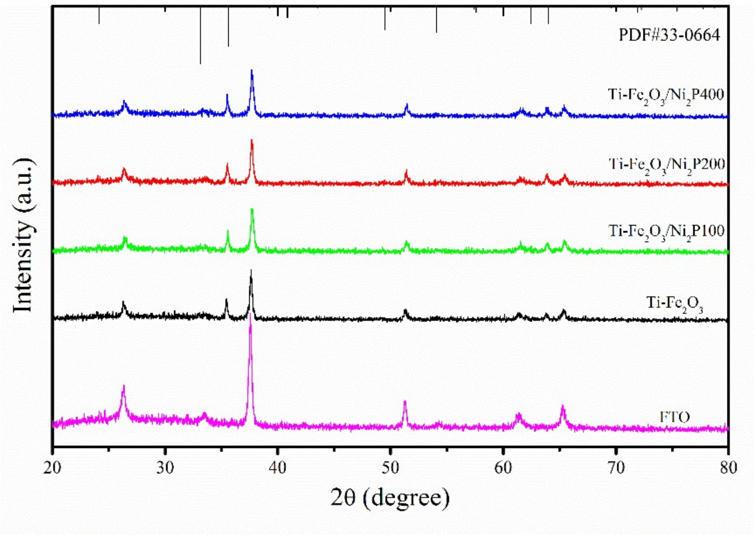

Figure S2. XRD patterns of FTO, Ti-Fe_2O_3, Ti-Fe_2O_3/Ni_2P100, Ti-Fe_2O_3/Ni_2P200 and Ti-Fe_2O_3/Ni_2P400 electrodes.

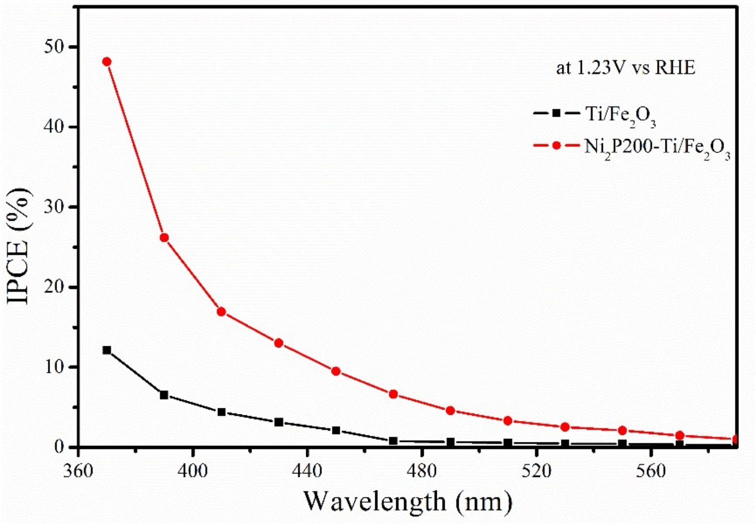

Figure S3. IPCE of the Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes in 1 M KOH electrolyte at 1.23 V vs. RHE.

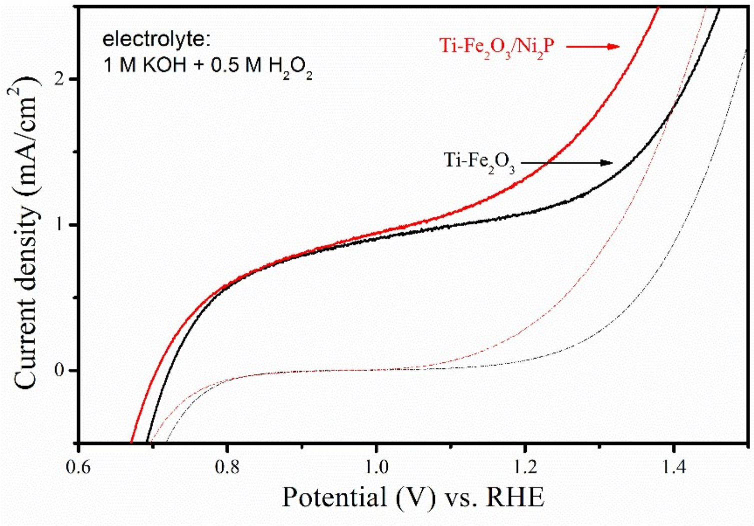

Figure S4. Photocurrent and dark current densities of Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes under 100 mW/cm^2 xenon light illumination in 1 M KOH + 0.5 M H_2O_2 electrolyte.

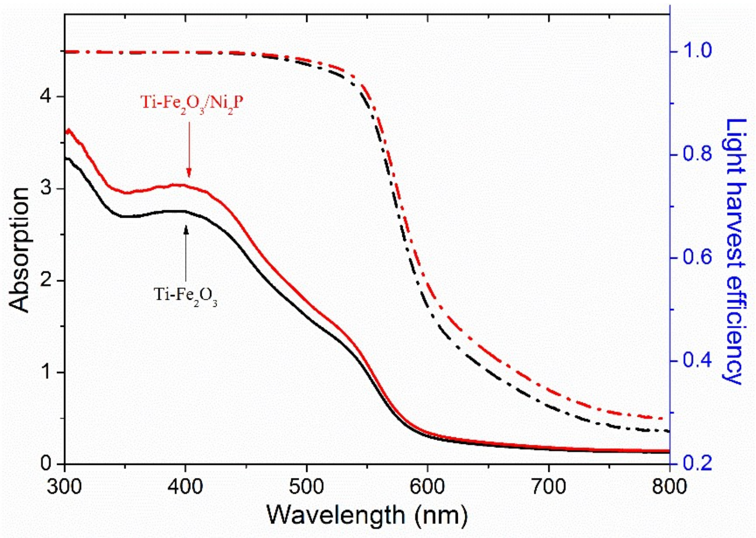

Figure S5. The absorption (solid line) and light harvest efficiency (dash line) of the Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes.

The light harvest efficiency (LHE) can be got from the absorption $A(\lambda)$[5,6]:

$LHE(\lambda)=1-10^{-A(\lambda)}$

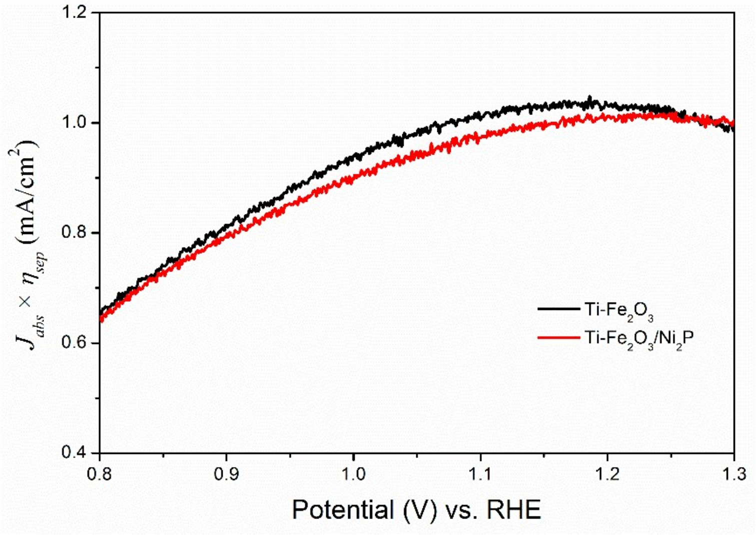

Figure S6. $J_{abs} \times \eta_{sep}$ vs. potential curves of Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes.

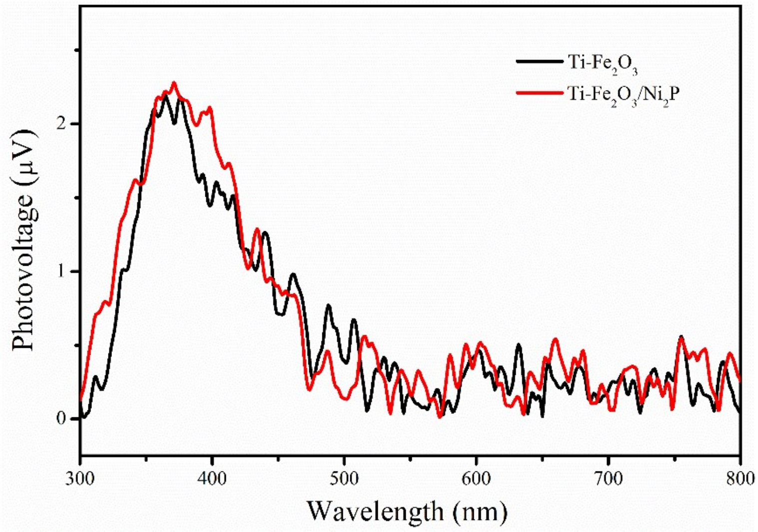

Figure S7. Surface photovoltage spectra of Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes.

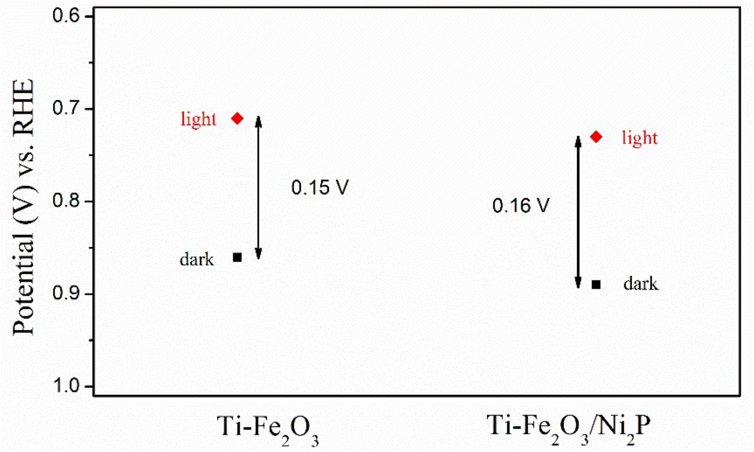

Figure S8. Open-circuit potentials (V_{OC}) of Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes measured in the dark (black) and under 100 mW/cm^2 xenon light illumination in 1 M KOH electrolyte. The open-circuit photovoltage (OPV) was calculated by the difference of V_{OC} values between dark and illumination conditions.

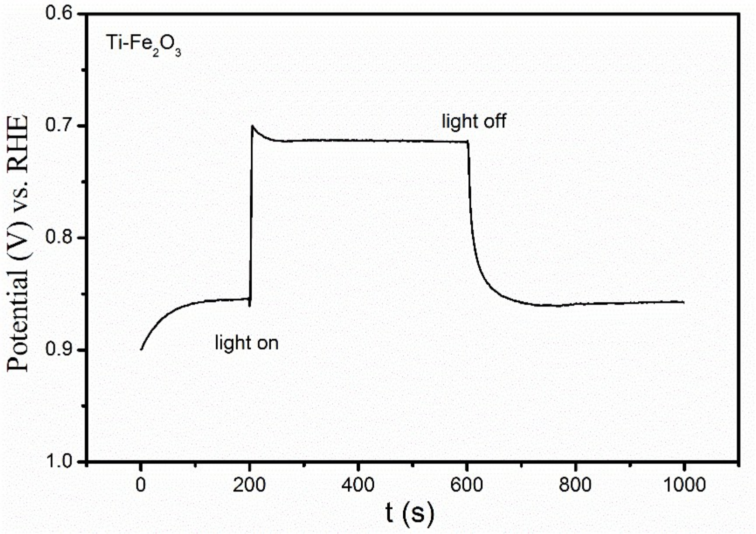

Figure S9. Transients recorded of open-circuit potentials (V_{OC}) measurement of Ti-Fe_2O_3 electrode in 1 M KOH electrolyte.

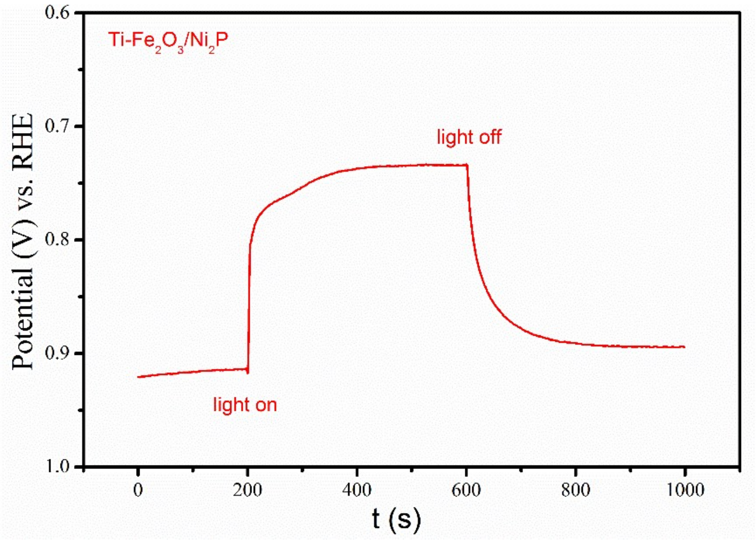

Figure S10. Transients recorded of open-circuit potentials (V_{OC}) measurement of Ti-Fe_2O_3/Ni_2P electrode in 1 M KOH electrolyte.

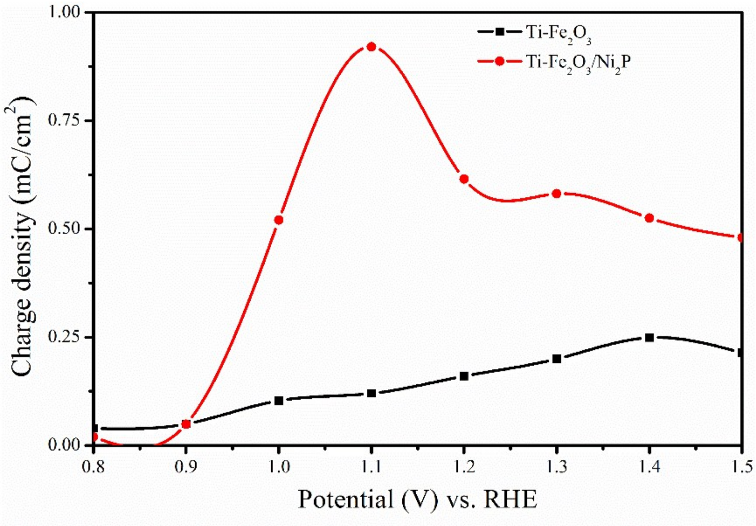

Figure S11. Accumulated charge density as a function of applied potentials of Ti-Fe_2O_3 and Ti-Fe_2O_3/Ni_2P electrodes, obtained by integration of the initial current spike.

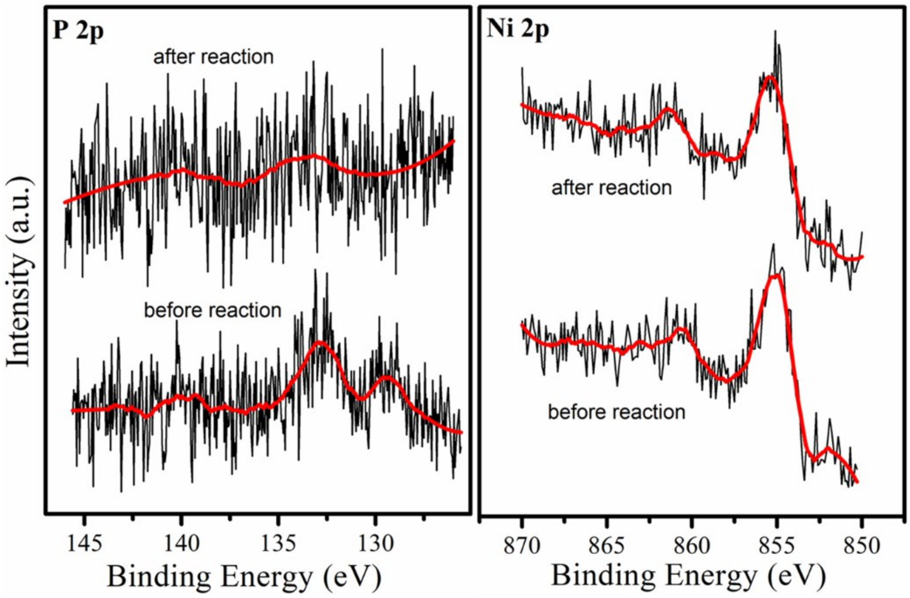

Figure S12. High-resolution Ni 2p and P 2p XPS spectra of Ti-Fe_2O_3/Ni_2P electrode before and after PEC process at a constant applied potential of 1.23 V vs. RHE in 1.0 M KOH for 2 h.

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