Ni$_2$P modified Ti$^{4+}$ doped Fe$_2$O$_3$ photoanode for efficient solar water oxidation by promoting hole injection

Qijing Bu,‡a Shuo Li,‡a Shuang Cao,b Qidong Zhao,c Yong Chen,b Dejun Wanga,d and Tengfeng Xie*a

a. College of Chemistry, Jilin University, Changchun 130012, P.R. (China).
b. Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry & University of Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100190, P. R. China
c. School of Petroleum and Chemical Engineering, Dalian University of Technology, Panjin 124221, P.R. (China).
d. Department of Chemistry, Tsinghua University, Beijing 100084, P.R. (China).

‡ These authors contributed equally to this work.
EXPERIMENTAL SECTION

1. Preparation of Samples

Preparation of Ti-Fe₂O₃ photoanodes: Ti-Fe₂O₃ photoanodes were fabricated according to our previous report.¹ Typically, 1 mL 0.05% (volume percentage) TiCl₄ (99%, Sinoreagent Co., Ltd) ethanol solution was added in 30 ml aqueous solution containing 0.15M FeCl₃·6H₂O (99%, Aladdin) and 1M NaNO₃ (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-Fe₂O₃ film was thoroughly washed by deionized water and annealed in air at 550 ºC for 2 h.

Preparation of Ni₂P nanoparticles: Ni₂P nanoparticles were synthesized according to our previous report.²

Preparation of Ti-Fe₂O₃/Ni₂P photoanodes: A drop-casting technique was used to synthesize the Ti-Fe₂O₃/Ni₂P photoanodes.³ Firstly, 2 mg of Ni₂P 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-Fe₂O₃ photoanodes. The drop-casted area was controlled to be 2.5 cm² and the mass of the Ni₂P was adjusted by the drop volume of “ink”. The composites were fully dried at 80 ºC for 1 h. In order to investigate the effects of Ni₂P loading on the photocatalytic activity, the Ti-Fe₂O₃/Ni₂P photoanodes with various drop volume (100µL, 200µL, 400µL) were prepared (respectively denoted as Ti-Fe₂O₃/Ni₂P100, Ti-Fe₂O₃/Ni₂P200, Ti-Fe₂O₃/Ni₂P400).

Note: If not specially indicated, the Ti-Fe₂O₃/Ni₂P represent Ti-Fe₂O₃/Ni₂P200 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 (\(\lambda = 1.5418 \text{ Å}\)) at 50 kV and 200 mA in the 20 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. 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 Al\(K\alpha\) 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:

\[E_{\text{RHE}} = E_{\text{Ag/AgCl}} + 0.0591 \times \text{pH} + 0.1976V\]

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:

\[IPCE = \frac{J \times 1240}{P_{\text{mono}} \lambda}\]
where \( J \) is the photocurrent density (mA cm\(^{-2}\)), \( P_{\text{mono}} \) is the light power intensity (mW cm\(^{-2}\)) of the monochromatic light, and \( \lambda \) is the wavelength of incident light (nm).

To examine the injection efficiency (\( \eta_{\text{inj}} \)), 0.5 M H\(_2\)O\(_2\) was added to the electrolyte solution because the oxidation of H\(_2\)O\(_2\) is thermodynamically and kinetically more favorable than water. When the photocurrent is recorded in the KOH/H\(_2\)O\(_2\) electrolyte, it is believed that PEC performance of the electrode is independent of the kinetic of the surface reaction. The injection efficiency (\( \eta_{\text{inj}} \)) were calculated using the following equation:

\[
\eta_{\text{inj}} = \frac{J_{\text{PEC}}}{J_{\text{H}_2\text{O}_2}}
\]

where \( J_{\text{PEC}} \) is the water splitting photocurrent, \( J_{\text{H}_2\text{O}_2} \) photocurrent obtained in KOH/H\(_2\)O\(_2\) 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:

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

Where the \( C \) is the capacitance of the space charge region, \( \varepsilon_0 \) is the vacuum permittivity, \( \varepsilon \) is the dielectric constant of \( \alpha\)-Fe\(_2\)O\(_3\), \( e \) 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:

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

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$_2$O$_3$, Ti-Fe$_2$O$_3$/Ni$_2$P100, Ti-Fe$_2$O$_3$/Ni$_2$P200 and Ti-Fe$_2$O$_3$/Ni$_2$P400 electrodes under 100 mW/cm$^2$ xenon light illumination in 1 M KOH electrolyte.

The Ti-Fe$_2$O$_3$/Ni$_2$P200 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$_2$O$_3$, Ti-Fe$_2$O$_3$/Ni$_2$P100, Ti-Fe$_2$O$_3$/Ni$_2$P200 and Ti-Fe$_2$O$_3$/Ni$_2$P400 electrodes.
Figure S3. IPCE of the Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$/Ni$_3$P electrodes in 1 M KOH electrolyte at 1.23 V vs. RHE.
Figure S4. Photocurrent and dark current densities of Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$/Ni$_2$P electrodes under 100 mW/cm$^2$ xenon light illumination in 1 M KOH + 0.5 M H$_2$O$_2$ electrolyte.
Figure S5. The absorption (solid line) and light harvest efficiency (dash line) of the Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$/Ni$_2$P electrodes.

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

$LHE(\lambda) = 1 - 10^{-A(\lambda)}$
Figure S6. $J_{abs} \times \eta_{ap}$ vs. potential curves of Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$/Ni$_2$P electrodes.
Figure S7. Surface photovoltage spectra of Ti-Fe₂O₃ and Ti-Fe₂O₃/Ni₃P electrodes.
Figure S8. Open-circuit potentials ($V_{OC}$) of Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$/Ni$_2$P 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$_2$O$_3$ electrode in 1 M KOH electrolyte.

Figure S10. Transients recorded of open-circuit potentials ($V_{OC}$) measurement of Ti-Fe$_2$O$_3$/Ni$_2$P electrode in 1 M KOH electrolyte.
Figure S11. Accumulated charge density as a function of applied potentials of Ti-Fe$_2$O$_3$ and Ti-Fe$_2$O$_3$/Ni$_2$P electrodes, obtained by integration of the initial current spike.
Figure S12. High-resolution Ni 2p and P 2p XPS spectra of Ti-Fe$_2$O$_3$/Ni$_2$P 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.

REFERENCES