Photoelectrochemical Properties of MOF Induced Surface Modified TiO2 Photoelectrode

<table>
<thead>
<tr>
<th>Journal</th>
<th>Nanoscale</th>
</tr>
</thead>
<tbody>
<tr>
<td>Manuscript ID</td>
<td>NR-ART-08-2018-006471.R1</td>
</tr>
<tr>
<td>Article Type</td>
<td>Paper</td>
</tr>
<tr>
<td>Date Submitted by the Author</td>
<td>25-Sep-2018</td>
</tr>
</tbody>
</table>
| Complete List of Authors | Feng, Pingyun; University of California, Department of Chemistry  
Jiao, Wei; Fudan University, Department of Chemistry  
Zhu, Jiaxing; Fudan University, Department of Chemistry  
Ling, Yun; Fudan University, Chemistry  
Deng, Mingli; Fudan University, Chemistry  
Zhou, Yaming; Fudan University, Chemistry Department |
Heteroatom doping and surface modification with other oxides are both important strategies to improve the photoelectrochemical (PEC) activities of TiO$_2$ photoelectrode. However, it is difficult to simultaneously combine the two strategies together in one synthesis process. Here, a simple one-pot synthetic method is developed to simultaneously modify TiO$_2$ photoelectrode surface by N-doping and surface modification with In$_2$O$_3$ and NiO. This method is achieved by growing MOF with N-containing organic ligand and In and Ni salts as metal precursors onto TiO$_2$ surface, followed by heat treatment at 600 °C. The roles of heteroatom doping and oxides modification are proposed as (i) N-doping extends the absorption edge of the TiO$_2$ to longer wavelength region and enhances the visible light absorption. (ii) N-doping together with the passivation of TiO$_2$ surface trap states by oxides modification increase the donor density in the TiO$_2$. (iii) Generated suitable interfaces on the surface of TiO$_2$, that facilitate photogenerated charge separation and transfer. In comparison with the pristine TiO$_2$ photoelectrode, the metal oxides and heteroatom modified TiO$_2$ photoelectrode exhibits superior photoelectrochemical performance under both simulated sunlight and visible light illumination. Suitable substrate of the electrode, appropriate size of the synthesized MOF precursors, choice of ligands and metal irons are all important factors for this strategy.

Photocurrents of the pristine TiO$_2$ improved photoelectrochemical activities. For example: Li et al. treated TiO$_2$ nanowires with hydrogen to form oxygen vacancies on the surface of TiO$_2$. With the increase of the donor density, these oxygen vacancies enhanced the photocurrent of TiO$_2$ photoelectrode. Mullins et al. synthesized N-modified TiO$_2$ nanowires with cobalt as a co-catalyst. By doping and co-catalyst modification, the photoelectrochemical performance was enhanced both in ultraviolet and visible light region. Lin et al. deposited Cu$_2$O on the surface of TiO$_2$ nanotube arrays to form the p-n junction. As a result, the separation of photoinduced holes and electrons was improved and the Cu$_2$O/TiO$_2$ hybrid photoelectrode exhibited superior performance. So far, great progress has been made in TiO$_2$ surface modification. However, modifying TiO$_2$ surface with multiple heteroatom and metal oxides simultaneously is still a challenge task for specific application.

Metal organic frameworks (MOFs) are a type of porous materials with unique atomic ordering. MOFs can be constructed with different organic ligands and metal ions. Because of their diverse chemical compositions and tunable structures, these MOFs are considered to be promising materials for many applications, including CO$_2$ capture, catalysis and energy conversion and storage. The flexible chemical composition of MOFs also makes them ideal precursors for modifying the surface of TiO$_2$ photoelectrode with complex composition and structure for different functionalities. From the synthetic point view, with MOF as a precursor to induce surface modification of TiO$_2$ for improving the photoelectrochemical properties, two key strategies need to be considered. One is the synthesis of a suitable TiO$_2$ substrate for hosting MOF material; The second one is to deposit MOFs precursors with proper metallic and
nonmetallic elements on the surface. With the above consideration, firstly, we synthesized a Ti\(^{3+}\) doped TiO\(_2\) substrate. The existence of Ti\(^{3+}\) could lead to more surface defect and this may enhance the interaction of the ligands in the MOF precursor solution and TiO\(_2\) surface. Secondly, we choose to deposit a MOF with In and Ni metal ions, and 1,2,4-triazolate as the ligand which contained N atom. Our strategy is to construct Ti\(^{3+}\) and N co-doped TiO\(_2\) combined with the deposition of specific metal oxides on the surface to enhance the light absorption and to construct the suitable interfaces (TiO\(_2\)/In\(_2\)O\(_3\)/NiO) to promote the separation of photogenerated electron-hole pairs for the TiO\(_2\) photoelectrode.

With the above strategies, metal oxides and heteroatom modified TiO\(_2\) based photoelectrode named as InNi-N/TiO\(_2\) was successfully synthesized. The loading status of the MOF precursors could be controlled by varying the synthesis conditions. The modification derived with MOF of different chemical compositions helps in tuning the surface electronic structure, properties of charge separation and transfer and photoelectrochemical activities of TiO\(_2\). Compared to the pristine TiO\(_2\) photoelectrode, the photoelectrochemical performance of InNi/N/TiO\(_2\) photoelectrode was enhanced obviously.

Results and discussion

The synthetic process for making InNi/N/TiO\(_2\) is illustrated in scheme 1. Firstly, the Ti\(^{3+}\) doped rutile TiO\(_2\) electrode was synthesized using a modified procedure from our previous work. Then, the TiO\(_2\) electrode was immersed into the solution containing MOF precursors (In\(^{3+}\), Ni\(^{2+}\), 1,2,4-triazolate and terephthalic acid). With a subsequent solvothermal treatment, the InNi-MOF grew on the surface of TiO\(_2\) (InNi-MOF/TiO\(_2\)). After a thermal treatment at 600 °C in N\(_2\) atmosphere, InNi-MOF was decomposed and the In\(_2\)O\(_3\) and NiO modified rutile TiO\(_2\) electrode with co-doping of N and Ti\(^{3+}\) was obtained.

The X-ray diffraction (XRD) patterns of TiO\(_2\) electrode, InNi-MOF/TiO\(_2\) electrode and InNi/N/TiO\(_2\) electrode are shown in Fig. 1. The as-prepared TiO\(_2\) on the surface of the Ti foil is rutile TiO\(_2\). The XRD pattern of InNi-MOF/TiO\(_2\) is shown in Fig. 1a. The diffraction peak at 8.8° and 12.8° can be indexed to (00-2) and (-120) facets of InNi-MOF, which confirm the formation of InNi-MOF on the surface of TiO\(_2\). In comparison, the XRD (Fig. 1b) of the electrode annealed at 600 °C (InNi/N/TiO\(_2\)) shows no other phases except for the rutile TiO\(_2\) and Ti metal. This is because the small amount of oxides derived from the pyrolysis of the InNi-MOFs is blow the measurable limit of XRD characterization.

Fig. 1 XRD patterns of (a) TiO\(_2\) electrode and InNi-MOF/TiO\(_2\), (b) InNi/N/ TiO\(_2\) and TiO\(_2\) electrode annealed at 600 °C.

The scanning electron microscopy (SEM) images of TiO\(_2\) electrode are shown in Fig. S1, which show most of the rutile TiO\(_2\) crystals grown on the Ti foil are rectangular pyramids with four \{110\} facets in the middle parts and four \{111\} facets on the top of the crystals. The surfaces of the rectangular pyramids are very smooth without any other clusters or particles on them. The corresponding cross-sectional views of TiO\(_2\) electrode in Fig. S1b and d show the rectangular pyramid morphology of TiO\(_2\) and the interface between the TiO\(_2\) and Ti foil substrate clearly. The thickness of TiO\(_2\) layer is about 2 µm. The SEM image and corresponding elemental mapping of InNi-MOF/TiO\(_2\) electrode in Fig. 2a show homogeneous distribution of Ti, In and Ni, which indicates that the InNi-MOF particles are distributed uniformly on the TiO\(_2\) electrode. As shown in Fig. 2b and c, the InNi-MOF nanoparticles with particle sizes from 20 nm to 100 nm were deposited on

![Scheme 1. Schematic illustration of the one-step synthesis of an InNi-MOF modified rutile TiO\(_2\) and its derived In\(_2\)O\(_3\), NiO and N modified rutile TiO\(_2\).](image-url)
the facet of the TiO$_2$ after the growth process of InNi-MOF. MOFs
crystals usually have large size of about several micrometers, which is
disadvantageous for the light absorption of TiO$_2$ and the
transportation of the carriers. By reducing the precursor
concentration and reaction time in the MOF synthesis, the InNi-MOF
particles grown on the surface of TiO$_2$ have much small size. These
small sizes could be helpful in the construction of suitable
heterostructures for improving the performance of electrode. By
annealing at 600 °C under N$_2$ flow, the In$_2$O$_3$ and NiO nano-particles
are formed on the surface of TiO$_2$ as shown from the SEM images in
Fig. 3. The SEM image and corresponding elemental mapping of
InNi/N/TiO$_2$ electrode in Fig. 3a also show homogeneous signals for Ti,
In and Ni, which demonstrates the uniform distribution of In$_2$O$_3$ and
NiO on the surface of TiO$_2$ after heat treatment. In Fig. 3b and e, it is
shown that the In$_2$O$_3$ and NiO decomposed from the InNi-MOF are all
nano-particles with smaller particle sizes than the InNi-MOF. The
transmission electron microscopy (TEM) images of nano-particles
grown on the TiO$_2$ were shown in Fig. 3c and f. The sizes of the
particles are about 15 nm to 40 nm as shown in Fig. 3c. The high-
resolution TEM image (the inner part of the white box in Fig. 3c) in Fig.
3e confirms that the particles are consist of two kinds of oxides: In
and NiO. As shown from the TEM images in Fig. 3, the particles
grows on the TiO$_2$ crystals usually have large size of about several
micrometers, which is disadvantageous for the light absorption of
TiO$_2$ and the transportation of the carriers. By reducing the precursor
concentration and reaction time in the MOF synthesis, the InNi-MOF
particles grown on the surface of TiO$_2$ have much small size. These
small sizes could be helpful in the construction of suitable
heterostructures for improving the performance of electrode. By
annealing at 600 °C under N$_2$ flow, the In$_2$O$_3$ and NiO nano-particles
are formed on the surface of TiO$_2$ as shown from the SEM images in
Fig. 3. The SEM image and corresponding elemental mapping of
InNi/N/TiO$_2$ electrode in Fig. 3a also show homogeneous signals for Ti,
In and Ni, which demonstrates the uniform distribution of In$_2$O$_3$ and
NiO on the surface of TiO$_2$ after heat treatment. In Fig. 3b and e, it is
shown that the In$_2$O$_3$ and NiO decomposed from the InNi-MOF are all
nano-particles with smaller particle sizes than the InNi-MOF. The
transmission electron microscopy (TEM) images of nano-particles
grown on the TiO$_2$ were shown in Fig. 3c and f. The sizes of the
particles are about 15 nm to 40 nm as shown in Fig. 3c. The high-
resolution TEM image (the inner part of the white box in Fig. 3c) in Fig.
3e confirms that the particles are consist of two kinds of oxides: In$_2$O$_3$
with a size of around 20 nm and NiO with a size of around 5 nm. The
distinct lattice spacings of 0.29 nm and 0.21 nm observed in the two
particles corresponds to In$_2$O$_3$ (222) and NiO (200), respectively. The
TEM images of In$_2$O$_3$, NiO and TiO$_2$ are shown in Fig. 3d and g. It is
clearly indicated that the In$_2$O$_3$ and NiO particles are grown on the
surface of TiO$_2$ and there is a good connection between the interface
of TiO$_2$ and In$_2$O$_3$ or NiO particles for the designed in-situ growth
process, which is beneficial for the transfer of carriers.

Fig. 3 (a) Low magnification SEM image and responding elemental
mapping, (b, e) high magnification SEM images of InNi/N/TiO$_2$, (c) TEM
image and (f) HRTEM image of In$_2$O$_3$ and NiO particles, (d, g) TEM
images of InNi/N/TiO$_2$.

Fig. 4 XPS spectra of (a) Ni 2p, (b) N 1s, (c) In 3d in InNi/N/TiO$_2$ and (d)
Ti 2p in the InNi/N/TiO$_2$ and the pristine TiO$_2$.

The surface chemical state of the InNi/N/TiO$_2$ is determined by the
X-ray photoelectron spectroscopy (XPS) as shown in Fig. 4. High
resolution XPS spectrum of the Ni 2p in Fig. 4a reveals that the two
peaks at 855.5 and 873.5 eV originate from Ni 2p$_{3/2}$ and 2p$_{1/2}$ of NiO
on the surface of TiO$_2$24, 25 respectively. The binding energies of 861.5
and 879.9 eV are identified as the satellite peaks of Ni 2p$_{3/2}$ and 2p$_{1/2}$
of NiO. As shown in Fig. 4c, the binding energy at 444.6 and 452.1 eV
originate from the In 2p$_{3/2}$ and 2p$_{1/2}$ in In$_2$O$_3$26 respectively. The N 1s
signal detected in Fig. 4b confirms the existence of N species in
InNi/N/TiO$_2$. The binding energy ranging from 401 to 398 eV suggests
the interstitial incorporated of N in TiO$_2$ and minor molecularly
chemisorbed N$_2$ species exist.27, 28 The atomic percentages of
nitrogen, indium and nickel in InNi/N/TiO$_2$ are 1 %, 3.5 % and 1.2 %,
respectively.

In comparison to the UV-visible absorption spectra of pristine TiO$_2$,
the InNi/N/TiO$_2$ did show a red shift as shown in Fig. 5a. In addition,
the light absorption in the visible light region (450 nm to 800 nm) is
also enhanced due to the existence of In$_2$O$_3$ and NiO on the surface
of TiO$_2$ compared to the pristine TiO$_2$.29, 30 It is worth noting that the
similar absorption bands of InNi/N/TiO$_2$ and TiO$_2$ from 420 nm to 800
nm, which are attributed to Ti$^{3+}$ confirm the existence of Ti$^{3+}$ in
InNi/N/TiO$_2$ because of the protection of nitrogen atmosphere in the
heat treatment process. According to the plot of transformed
Kubelka-Munk function in Fig. 5b, the bandgap of InNi/N/TiO$_2$ is
reduced to 2.88 eV, compared to the bandgap of 3.03 eV of the
pristine TiO$_2$. By heteroatom doping and surface modification with
different oxides, the surface electronic structure of the InNi/N/TiO$_2$
was adjusted successfully.
The photoelectrochemical activities of the InNi/N/TiO$_2$ photoelectrode and pristine TiO$_2$ photoelectrode were tested in a standard three-electrode electrochemical cell, using Pt foil as the counter electrode, a saturated calomel electrode (SCE) as the reference electrode and 0.5 M Na$_2$SO$_4$ (pH=6.3) as the electrolyte. The linear sweeps were firstly measured under 100 mW/cm$^2$ simulated sunlight illumination from a 150 W Xenon lamp coupled with a AM 1.5G filter (see details in the experimental section). As shown in Fig. 6a, a obviously enhanced photocurrent was observed for the InNi/N/TiO$_2$. The photocurrent density of the InNi/N/TiO$_2$ photoelectrode is 1.28 mA/cm$^2$ at 0.6 V vs SCE, which is 2.7 times higher than that of the pristine TiO$_2$ photoelectrode. Moreover, compared with the pristine TiO$_2$ photoelectrode, the onset potential of the InNi/N/TiO$_2$ photoelectrode is decreased by about 73 mV, which could be contributed from the surface modification of the oxides. The transient photocurrents of InNi/N/TiO$_2$ photoelectrode and pristine TiO$_2$ photoelectrode at 0.6 V vs SCE are shown in Fig. 6b, the current densities for InNi/N/TiO$_2$ photoelectrode and pristine TiO$_2$ photoelectrode are 1.29 mA/cm$^2$ and 0.45 mA/cm$^2$, which match well with the data of linear sweep voltammograms. More importantly, the InNi/N/TiO$_2$ photoelectrode shows better performance under visible light irradiation (> 400 nm, details in the experimental section) than that of the pristine TiO$_2$ as shown in Fig. 6c. Because the co-doping of N and Ti$^{3+}$ in the TiO$_2$ induced visible-light absorption, the photocurrent at 0.6 V vs SCE for InNi/N/TiO$_2$ photoelectrode increases from 52 µA/cm$^2$ to 101 µA/cm$^2$, comparing with the pristine TiO$_2$ photoelectrode. In addition, we also measured the time-dependent photocurrent at 0.6 V under 100 mW/cm$^2$ simulated sunlight illumination (shown in Fig. 6d), which shows no significant attenuation of the photocurrent in about 4 hours, suggesting the excellent stability of the InNi/N/TiO$_2$ photoelectrode.

Incident-photon-current-conversion efficiency (IPCE) is conducted to compare the conversion efficiency for different photoelectrodes under standard light source irradiation. IPCE can be expressed by the following equation:

$$\text{IPCE} = \frac{1240 \times J}{\lambda \times E(\lambda)} \times 100\%$$

(1)

Where the $J$ is the obtained photocurrent density at a specific incident wavelength, the $\lambda$ is the wavelength of incident light, and the $E(\lambda)$ is the irradiance at a specific incident wavelength. We measured the IPCE on the InNi/N/TiO$_2$ photoelectrode and pristine TiO$_2$ photoelectrode at 0.6 V vs SCE, which are shown in Fig. 7. The maximum IPCE of InNi/N/TiO$_2$ photoelectrode is 83.2 % at 340 nm, which is about 1.4 times higher than that of pristine TiO$_2$ photoelectrode. It shows that the InNi/N/TiO$_2$ photoelectrode exhibits
obviously improved IPCE over UV region. Significantly, the IPCE of InNi/N/TiO₂ photoelectrode from 400 to 420 nm is also much higher than that of pristine TiO₂ photoelectrode. It suggests that modification with N and metal oxides is an efficient method to improve the performance of TiO₂ photoelectrode in both UV and visible region.

To further investigate how the surface modification enhanced the charge transfer and separation, the Mott–Schottky plots and electrochemical impedance spectroscopy (EIS) of InNi/N/TiO₂ photoelectrode and pristine TiO₂ photoelectrode were conducted. As shown in Fig. 8a, the Mott–Schottky plots of both InNi/N/TiO₂ and pristine TiO₂ were collected with a bias of 0.6 V vs SCE at 1 KHz under AM 1.5G irradiation (100 mW/cm²). The positive slopes in the plots are consistent with the N-type semiconductor. The Mott-Schottky plots are given by the equation: 1/C² = 2(E-E₀)/εε₀kT/εNₑ* where the C is the interfacial capacitance, E is the applied bias, k is the Boltzmann constant, the t is the absolute temperature, ε is the electronic charge, ε is the dielectric constant of the semiconductor and ε₀ is the permittivity of free space. The equation can be used to calculate the donor density (Nₑ) from the E₀ and the value of the slope. The InNi/N/TiO₂ photoelectrode shows a smaller slope and more negative E₀ compared to these of the pristine TiO₂ photoelectrode, according to the equation above, which indicated an increased donor density in the InNi/N/TiO₂ photoelectrode. The N-doping could enhance the Ti³⁺ states, which is regarded as a kind of donor-type impurity in TiO₂. Besides, deposition of oxides on the surface of TiO₂ could passivate the trap states to prevent from acting as the charge trap centers. For these two reasons, the carrier concentration was increased and thereby the conductivity of the electrode was improved.

It is interesting that the flat band potential (Eᶠᵇ) of InNi/N/TiO₂ photoelectrode shifted to a more negative potential at -0.79 V vs SCE compared to the Eᶠᵇ of pristine TiO₂ at -0.58 V vs SCE. It is probably caused by the deposition of oxides on the surface of TiO₂. The negative shift of Eᶠᵇ facilitates the efficiency of charge carriers separation by increasing the degree of band bending to accelerate the migration of electrons and holes to the different directions at the interface. The Mott-Schottky plots of InNi/N/TiO₂ photoelectrode exhibits another Eᶠᵇ at -1.1 V vs SCE. It could be related to the different surface states from the deposited In₂O₃ and NIO or N and Ti³⁺ co-doping on the surface of TiO₂.

Charge transfer properties of InNi/N/TiO₂ photoelectrode and pristine TiO₂ photoelectrode under illumination were characterized by electrochemical impedance spectroscopy. EIS measurements were carried out with a bias of 0.6 V vs SCE from 0.1 Hz to 10⁵ Hz under AM 1.5G illumination. Fig. 8b displays the Nyquist plots of InNi/N/TiO₂ photoelectrode and pristine TiO₂ photoelectrode respectively. Both InNi/N/TiO₂ photoelectrode and pristine TiO₂ photoelectrode show a single capacitive arc. The diameters of two arcs are related to the charge transfer resistance in the charge transfer process. InNi/N/TiO₂ photoelectrode exhibits an arc with a smaller diameter than that of pristine TiO₂ photoelectrode under irradiation suggesting that the InNi/N/TiO₂ photoelectrode is more efficient in photogenerated charges transfer and separation.

According to the energy level distribution of TiO₂, In₂O₃ and NIO, the proposed interface energies of InNi/N/TiO₂ are illustrated in Fig. 9. As shown in Fig. 9a, the work functions of TiO₂, In₂O₃ and NIO are about 4.2 eV, 4.4 eV and 5.3 eV respectively according to previous literature. On the InNi/N/TiO₂ photoelectrode, as shown in Fig. 9b, the energy bands of rutile TiO₂ bend upward and In₂O₃ bend downward on the interface of TiO₂ and In₂O₃. The energy bands of In₂O₃ bend upward and NIO bend downward on the In₂O₃ and NIO interface (Fig. 9b). As a result of the band bending, the transfer of photo-induced electrons from TiO₂ to In₂O₃ and NIO is difficult because of the potential barrier between both the interfaces of TiO₂ and In₂O₃ and the In₂O₃ and NIO. The photoinduced electrons have a great tendence to transfer from TiO₂ to Ti foil, and then to the counter electrode. In addition, the band bending could favor the transfer of photo-induced holes from TiO₂ to In₂O₃ and NIO. The analysis above suggests that suitable choice of the metal oxide components could improve the photoelectrochemical properties of TiO₂ photoelectrode by constructing the interfaces that is favorable for the transfer and separation of the photo-induced carriers, which is supported well by the experimental results.
time resulted in large sized In$_2$O$_3$ and NiO, which is disadvantage for the homogeneous distribution of metal oxides on the surface of TiO$_2$. A suitable size of the metal oxides controlled by the growth conditions of the MOF precursor is a key factor for the improved activity of the photoelectrode. Fig. S4 shows the photocurrent tested from InNi/N/TiO$_2$ photoelectrode annealed at different temperatures (400 °C, 500 °C, 600 °C, 700 °C), which indicated that the 600 °C is the best temperature for the heat treatment.

**Experimental**

**Synthesis of TiO$_2$ photoelectrode**

The TiO$_2$ photoelectrode was synthesized based on the previous work. A 1×2 cm Ti foil (0.25 mm thickness, 99.5 % trace metal, Alfa Aesar) was cleaned by sonication in ethanol, acetone, isopropanol and deionized water separately. Then the clean Ti foil was placed in a teflon-lined stainless steel autoclave which contained 10 mL aqueous HCl solution (0.45 M), and treated at 220 °C for 12 h. After reaction, the product was collected and washed with deionized water several times. A blue film was grown on the surface of the Ti foil. The TiO$_2$ photoelectrode prepared from the above procedures was placed in a teflon-lined stainless steel autoclave containing 10 mL aqueous N$_2$H$_4$ solution (20 % by weight). The autoclave was heated at 220 °C for 20 h. Then, the product was collected and washed with deionized water several times.

**Synthesis of modified TiO$_2$ photoelectrodes**

33.4 mg indium chloride (InCl$_3$), 24.4 mg nickel (II) chloride hexahydrate (NiCl$_2$•6H$_2$O), 26 mg terephthalic acid (C$_8$H$_4$O$_4$) and 10 mg 1,2,4-triazole (C$_2$H$_4$N$_3$) were added into a 20 mL glass vial containing a mixed solvent of 4 g N,N-Dimethylmethanamide (C$_3$H$_6$N$_2$O) and 0.8 g deionized water. After stirring for 30 min, the TiO$_2$ photoelectrode was immersed into the solution for 30 min. Then, the vial was sealed and treated at 120 °C for 6 h. After reaction, the TiO$_2$ electrode was collected and washed with deionized water and ethanol for several times. Then, the samples were dried by Ar flow. At last, the photoelectrode was treated in a furnace at 600 °C with N$_2$ flow for 2 h.

**Characterization**

X-ray diffraction (XRD) patterns of the samples were recorded on Bruker D8 powder diffractometer using Cu irradiation. Morphologies and structures of the prepared samples were further examined with a Philips Nova NanoSEM450 scanning electron microscope (SEM). Transmission electron microscope (TEM) and High-resolution Transmission electron microscope (HRTEM) images were obtained with a JEM 2100F field emission gun transmission electron microscope operated at an accelerating voltage of 200 kV. Chemical compositions and states of the TiO$_2$ samples were analyzed using X-ray photoelectron spectroscopy (XPS, Thermo Escalab 250Xi, a monochromatic Al K$_\alpha$ X-ray source). All binding energies were referenced to the C 1s peak (284.8 eV) arising from adventitious carbon.
carbon. The optical absorbance spectra of the samples were recorded in a shimadzu UV-3101PC UV-Vis-NIR spectrophotometer.

**Photoelectrochemical measurement**

Photoelectrochemical performance was investigated using solartron 1287 Electrochemical Workstation in a standard three-electrode cell with the TiO$_2$-based working electrode, a Pt foil counter electrode, and a saturated calomel reference electrode, respectively. The light source was a 150 W Xenon lamp (Newport, 69907) coupled with an AM 1.5G filter (Newport, 81094). Light intensity was adjusted to 100 mW/cm$^2$ with a radiant power meter (Newport, 70260) combined with a probe (Newport, 70268). 0.5 M Na$_2$SO$_4$ (pH=6.3) purged with Ar was used as the electrolyte. In addition, Xenon lamp with a filter (Newport, FR-GG400) was used to produce a visible light source below the wavelength of 400 nm. The incident photon to current efficiency (IPCE) was measured under the same xenon lamp equipped with a monochromator (Newport, 74404).

**Conclusions**

The conclusions we developed a simple one pot synthetic method that can combine the heteroatom doping strategy with surface modification of metal oxides on TiO$_2$ photoelectrode. The In$_2$O$_3$ and NiO modified rutile TiO$_2$ electrode with co-doping of N and Ti$^{3+}$ was obtained here. The co-doping of N and Ti$^{3+}$ to TiO$_2$ extended the absorption edge and enhanced the light absorption of TiO$_2$ in the visible region and increased the donor density. At the same time, the surface modification by In$_2$O$_3$ and NiO also passivated the surface trap states and constructed the appropriate interfaces for promoting the separation and transfer of photogenerated charges. Subsequently, the modified TiO$_2$ photoelectrode showed superior photoelectrochemical performance under both simulated sunlight (2.7 times) and visible light (near 2 times) illumination compared to the pristine TiO$_2$ photoelectrode. Suitable substrate of the electrode, appropriate size of MOF precursor and choice of ligands with metal ions all play important roles in improving the performance of the materials. The modification method shown here could potentially serve as a new promising way in the fabrication of high-performance PEC device for both TiO$_2$ and other types of semiconductors.

**Conflicts of interest**

There are no conflicts to declare.

**Acknowledgements**

The research is mainly supported by US Department of Energy, Office of Basic Energy Sciences, Materials Sciences and Engineering Division under Award No. DE-SC0010596 (P.F) (on the synthesis of MOF and electrochemical characterization). Dr. Wei Jiao thanks for the financial support of the NSFC (51402314) and China Postdoctoral Science Foundation (2016M601501) (on the SEM and XPS characterizations). The authors also thank Dr. Yangtao Zhou for his help in TEM characterization.

**References**


In$_2$O$_3$ and NiO modified rutile TiO$_2$ electrode with co-doping of N and Ti$^{3+}$