Boosting Photoelectrochemical Water Splitting Performance of Ta₃N₅ Nanorod Array Photoanodes by Forming a Dual Co-catalyst Shell

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Abstract
Concerning both the activity and stability of the promising solar-driven Ta\(_3\)N\(_5\)-based photoanodes for photoelectrochemical water splitting, the strategy for simultaneously promoting charge separation, enhancing catalytic activity and also improving the resistance to self-oxidation is highly desirable and actively pursued. In this study, a novel dual co-catalyst shell consisting of a continuous CoPi layer at the bottom and many non-continuous Co(OH)\(_2\) islands at the top of the CoPi layer is designed to meet the strict requirements for efficient Ta\(_3\)N\(_5\) photoanodes. As a result of the synergistic effects of such a shell in collectively addressing the concerns, the constructed photoanode of CoPi/Co(OH)\(_2\)-Ta\(_3\)N\(_5\) nanorod arrays show the remarkably enhanced photoelectrochemical water splitting performance compared with the photoanodes with single co-catalyst. The results demonstrated in this study are expected to shed some light on constructing efficient photoelectrodes of the light absorbers that have wide absorption range but low resistance to self-oxidation.
Introduction

Converting and storing abundant solar energy into chemical bonds (e.g. H₂) has been regarded as an effective route to address the emerging issues of energy shortage and environmental pollution. Solar driven water splitting in the photoelectrochemical (PEC) cells is considered as a classic scenario for this purpose, and has been intensively investigated in the past decades.[1-8] The core part of a PEC cell is its photoelectrode, which performs the tasks of capturing incident sunlight to produce photogenerated charge carriers and subsequent inducing water splitting on its surface. Consequently, the materials for the photoelectrodes need to meet both thermodynamic and kinetic requirements in order to efficiently achieve solar-driven water splitting spontaneously as follows: 1) a proper bandgap between 1.6 and 2.0 eV that is desirable for water splitting with the purpose of fully utilizing sunlight; 2) appropriate band edge positions that stride over the redox potentials of water splitting; 3) high carrier transport ability that can enable the photo-carriers effectively to arrive at the surface; 4) active surface that can promote water splitting. Among numerous photoelectrode materials, n-type Ta₃N₅ with a direct bandgap of around 2.1 eV is one of a few ideal materials that almost fulfill all aforementioned requirements.[9,10] The theoretical solar to hydrogen storage efficiency of Ta₃N₅ based photoanodes was determined to be over 16%.[11]

On the basis of various strategies, very encouraging progress in developing efficient Ta₃N₅-based photoanodes [12-21, 24-27] has been made in the past decade. Although a record photocurrent density of 12.1 mAcm⁻² that is very close to the theoretical value of 12.9 mAcm⁻² under AM1.5G simulated sunlight has been achieved in the PEC cell
with interface-engineered Ta3N5 photoanodes,[12] the open voltages obtained so far are still much lower than the theoretical value.[12-15] The poor stability caused by the non-corrosion surface chemical reactions is another limiting factor of Ta3N5 based photoanodes. The self-limiting surface oxidation of Ta3N5 in aqueous solution results in a thin amorphous layer containing abundant oxygen, which is proved to pin surface Fermi level and thus fully suppressing the photoactivity of Ta3N5.[16] Conformal coating of a thin layer of oxygen evolution reaction (OER) co-catalyst on Ta3N5 photoanode surface can play a dual role in improving both the open voltage and stability by lowering the OER barrier and introducing water-proof shell. Various OER co-catalysts including CoOx, Co(OH)2, CoOOH, “CoPi” and Fe-Co-Ni based compounds have been extensively explored to decorate Ta3N5 photoanodes for performance improvement.[13,14,17-28] The formed interfaces (Ta3N5/co-catalyst and co-catalyst/electrolyte) accompanying with co-catalyst decoration play an important role in promoting the photo-carrier transfer, suppressing surface self-oxidation and thus improving the PEC water splitting performance. The rational designing of the Ta3N5/co-catalyst interface has attracted increasing attention and many modifiers that do not act as co-catalyst have also been attempted to further enrich the interface properties. Hole-storage layers (HSLs), ferrihydrite layer and Ni(OH)x/ferrihydrite composite layer, formed at the Ta3N5/co-catalyst interface were demonstrated to be very effective in extracting photo-holes from Ta3N5 and delivering them to the OER co-catalysts.[12,14] Furthermore, a thin amorphous TiOx layer introduced at the Ta3N5/HSL interface can act as an electron blocking layer to suppress the photocarrier recombination. By
conducting these interface designs, a record efficiency of 2.5 % with high photocurrent density of 12.1 mAcm$^{-2}$ was achieved by Li’s group.[12] Alternatively, sequential deposition of co-catalysts with high hole-extraction ability and high OER activity is another effective strategy to facilitate interfacial transfer of photo-holes.[29] Co(OH)$_2$ has been recognized as an effective hole-extraction co-catalyst for Ta$_3$N$_5$ based photoanodes. Recently, the formation of interfacial Ta-O-Co bonds induced by the produced O$^*$ radicals under light irradiation was found to facilitate the photo-hole extraction for a high photocurrent density and good stability when high active OER co-catalyst “CoPi” was consecutively coated on the Ta$_3$N$_5$/Co(OH)$_2$ system.[30]

In this study, different from previous studies that used Co(OH)$_2$ as a photo-hole transfer bridge across the Ta$_3$N$_5$/CoPi interface,[27,30] we decorated Co(OH)$_2$ on the outermost surface of “CoPi” with the anticipation of enhancing the OER activity of “CoPi” to enable a better performance. Taking into account the potential advantages of one-dimensional array structures in capturing light, promoting charge separation and also modulating interface structures, the film of Ta$_3$N$_5$ nanorod arrays supported on Ta foil substrate was used as a platform to construct Co(OH)$_2$/CoPi-Ta$_3$N$_5$ photoanodes. Owing to the strong interaction between Co(OH)$_2$ and CoPi and enhanced OER activity at Co(OH)$_2$/CoPi/electrolyte three-phase boundaries, the resultant Co(OH)$_2$/CoPi-Ta$_3$N$_5$ photoanode shows the remarkably enhanced photocurrent density, open voltage and stability when compared with CoPi-Ta$_3$N$_5$ and Co(OH)$_2$-Ta$_3$N$_5$ photoanodes. The photocurrent density of the optimal Co(OH)$_2$/CoPi-Ta$_3$N$_5$ photoanode under AM 1.5G sunlight irradiation reaches 3.8 mA cm$^{-2}$ at 1.23 V versus reversible hydrogen electrode
(RHE) and over 90% the initial value after a 20 min duration test.

**Experimental section**

**Synthesis of Ta$_3$N$_5$ nanorod array films.** Ta$_3$N$_5$ nanorod arrays supported on Ta foil substrate were synthesized by a template-free vapor-based hydrothermal process and subsequent high-temperature nitridation method according to our previous report.[15] In detail, Ta foil (0.25 mm thick, Alfa Aesar) was ultrasonically cleaned in ethanol, acetone, isopropanol and deionized water each for 15 minutes in series. The cleaned Ta foil was suspended above 0.2 M HF aqueous solution in a Teflon-lined autoclave, and heated at 180 °C for 12 h to grow Ta$_2$O$_5$ nanorod arrays on the Ta foil. After the vapor-phase hydrothermal reaction, the sample was heated in a gaseous NH$_3$ atmosphere with a flow of 20 mL/min at 1000 °C for 6 h to form Ta$_3$N$_5$ nanorod arrays.

**The deposition of Co(OH)$_2$ on Ta$_3$N$_5$ nanorods.** The successive ionic layer adsorption and reaction method was used to deposit Co(OH)$_2$ nanoparticles onto the Ta$_3$N$_5$ nanorods. As-prepared Ta$_3$N$_5$ nanorod array photoanodes were immersed in an aqueous solution of 50 mM Co(CH$_3$COO)$_2$, deionized water, an aqueous solution of 100 mM NaOH and deionized water in turn each for 60 seconds to accomplish one cycle deposition of Co(OH)$_2$ nanoparticles. To get an optimal efficiency, five deposition cycles were repeated to load a desired amount of Co(OH)$_2$ nanoparticles on the nanorods.

**The deposition of CoPi on Ta$_3$N$_5$ nanorods.** Before the CoPi deposition, as-prepared nanorod array films were immersed in a mixed solution of HF:HNO$_3$:H$_2$O=1:2:7 in volume for tens of seconds and then rinsed with deionized water. The treated films were
deposited with CoPi cocatalysts by photo-assisted electrodeposition process,[13] which was conducted in a traditional three electrode photoelectrochemical cell (Ta₃N₅ photoelectrode as the working electrode, Ag/AgCl electrode as the reference electrode and a Pt foil as the counter electrode) with the electrolyte of 0.1 M potassium phosphate aqueous solution containing 0.5 mM Co(NO₃)₂ (pH = 7). During the 8 min photo-electrodeposition duration, a constant current density of 10 μA cm⁻² was kept and the light irradiation was provided by an AM 1.5G sunlight simulator. After the deposition, the photoelectrode was rinsed with deionized water. In addition, the further deposition of Co(OH)₂ on CoPi-Ta₃N₅ was conducted by the procedures used for the deposition of Co(OH)₂ on bare Ta₃N₅ described above.

**PEC water splitting measurement.** The photoelectrochemical water splitting test was carried out in a three electrode system, in which the Ta₃N₅ nanorod array photoanode was used as the working electrode, Ag/AgCl electrode as the reference electrode and a Pt foil as the counter electrode. And the electrolyte is 1 M NaOH aqueous solution and the light source is AM 1.5G simulated sunlight (Newport). According to the Nernst equation (E_RHE=E_{Ag/AgCl} + 0.059 pH + 0.196), the recorded bias vs. Ag/AgCl reference electrode can be converted to potentials referring to RHE. The wavelength dependent incident photon-to-current conversion efficiency (IPCE) was calculated according to the following equation: IPCE(%) = \[1240\times\text{photocurrent density (mA cm}^{-2}\)] / [ wavelength (nm) × photon flux (mW cm⁻²) ] × 100%

**Measurement of electrochemical impedance spectra.** The electrochemical impedance spectra of samples were measured with an electrochemical work station.
(Biologic VSP 300) at the potential of 1.23 V (vs. RHE) with a 10 mV amplitude perturbation and frequencies from 100 mHz to 1 MHz.

**Measurement of gaseous products produced in the PEC water splitting.** An airtight three-electrode PEC cell consisting of Co(OH)$_2$/CoPi-Ta$_3$N$_5$ photoanodes as the working electrode, Ag/AgCl electrode as the reference electrode and a Pt foil as the counter electrode was used for testing gas production. Prior to filling Ar gas in the cell to 5 kPa, the PEC cell was evacuated to less than 10 Pa. The PEC water splitting was conducted at 1.23 V vs. RHE in a stirred aqueous solution of 1 M NaOH under AM 1.5G simulated sunlight. The amount of hydrogen produced in the PEC cell was determined with a gas chromatograph (Agilent 6890N).

**Results and Discussion**

The successful synthesis of pure Ta$_3$N$_5$ phase was confirmed by X-ray diffraction (XRD) patterns of the as-prepared sample (Figure S1). No additional peaks appear in the XRD patterns after the deposition of CoPi and Co(OH)$_2$ as a result of the amorphous (or very low crystallinity) nature and low loading amount of these two components. Comparison of scanning electron microscopy (SEM) images of three modified Ta$_3$N$_5$ samples with pristine Ta$_3$N$_5$ (Figure 1a-c and Figure S2a) suggests no obvious change in the shape of the nanorods before and after the deposition of co-catalysts CoPi and/or Co(OH)$_2$, which indicates the conformal deposition of co-catalyst(s) on the Ta$_3$N$_5$ nanorods.

The microstructures of the nanorods in different samples were further characterized by recording transmission electron microscopy (TEM) images of single nanorod scraped from the Ta$_3$N$_5$ films. The nanorod from the pristine film has smooth surface
and a diameter of around 20 nm (Figure 1d). The corresponding high resolution TEM (HRTEM) image (Figure 1h) confirms the single crystalline nature of the nanorod and the lattice fringes with the spacing of 0.249 nm and 0.297 nm are corresponding to the (3-1-1) and (211) facets of Ta₃N₅, respectively. When CoPi was photo-deposited, an amorphous shell with a relatively uniform thickness of several nanometers was formed on the surface of the nanorod scraped from the CoPi modified Ta₃N₅ film (Figure 1e). The Ta₃N₅ nanorod and CoPi amorphous shell has a sharp interface and the single crystalline nature of the nanorod is well retained on the basis of the HRTEM image (Figure 1h). The uniformly and intimately coated CoPi shell has the dual functions of both extracting photo-holes and segregating Ta₃N₅ from water so that the performance and stability can be improved simultaneously. After subsequent deposition of Co(OH)₂ on the CoPi-Ta₃N₅ nanorods, additional particles with the size of several nanometers are randomly located on the outmost surface of the CoPi shell (Figure 1f). These small particles show blurry fringes with spacing of 0.276 nm and 0.178 nm (Figure 1i), which are associated with the (100) and (102) facets of Co(OH)₂. This suggests the formation of Co(OH)₂ nanoparticles on the outmost surface. Similar Co(OH)₂ nanoparticles are also observed on the Ta₃N₅ nanorods when Co(OH)₂ was directly deposited on the bare Ta₃N₅ nanorods (Figure S2b and c). In accordance with previous reports,[30] the Co(OH)₂ nanoparticles prepared by the successive ionic layer adsorption and reaction method are apt to form islands on the substrate. Such discontinuous shell consisting of the Co(OH)₂ islands is not effective in segregating Ta₃N₅ in the Co(OH)₂-Ta₃N₅ system from water. However, these Co(OH)₂ islands located on the uniform CoPi shell in
Co(OH)$_2$/CoPi-Ta$_3$N$_5$ can create numerous CoPi and Co(OH)$_2$ boundaries exposed. The strong interaction between the CoPi substrate and Co(OH)$_2$ nanoparticles might result in an enhanced OER catalytic activity at the boundaries.

**Figure 1.** SEM images of the films of (a) bare Ta$_3$N$_5$, (b) CoPi-Ta$_3$N$_5$ and (c) CoPi/Co(OH)$_2$-Ta$_3$N$_5$ nanorod arrays. TEM and HRTEM images recorded from single nanorod scraped from (d, g) bare Ta$_3$N$_5$, (e, h) CoPi-Ta$_3$N$_5$ and (f, i) CoPi/Co(OH)$_2$-Ta$_3$N$_5$ films, respectively.
Figure 2. HAADF image of single nanorod scraped from CoPi/Co(OH)$_2$-Ta$_3$N$_5$ film and corresponding Ta element, N element, Co element and P element EDS mapping images recorded from the single nanorod.

Figure 3. Schematic images of bare Ta$_3$N$_5$ nanorod arrays, CoPi decorated Ta$_3$N$_5$ nanorod arrays (CoPi-Ta$_3$N$_5$) and Co(OH)$_2$ decorated CoPi-Ta$_3$N$_5$ system (CoPi/Co(OH)$_2$-Ta$_3$N$_5$).
To further confirm the formation of isolated Co(OH)$_2$ islands on the well distributed CoPi shell, the elemental distribution images have been recorded on single nanorod scraped from the CoPi/Co(OH)$_2$-Ta$_3$N$_5$ film by TEM in the model of high angle annular dark-field (HAADF) with the help of energy dispersive spectrometer (EDS). The bright one-dimensional zone displayed in the HADDF image in Figure 2 (the left panel) corresponds to the CoPi/Co(OH)$_2$-coated Ta$_3$N$_5$ nanorod. Ta and N are two basic compositions of Ta$_3$N$_5$ so that their element mapping patterns duplicate the bright zone’s shape of the nanorod. The signal of Co in the pattern is contributed by both CoPi and Co(OH)$_2$ and it exhibits a similar distribution pattern to that of Ta and N elements. This confirms the conformal deposition of CoPi and Co(OH)$_2$ on the Ta$_3$N$_5$ nanorods. To separate the distribution of the Co(OH)$_2$ nanoparticles from CoPi, P element, an exclusive composition P of CoPi is mapped to monitor the distribution of CoPi. The well-distributed P element indicates a uniform shell of CoPi on the Ta$_3$N$_5$ nanorod. The distribution of Co(OH)$_2$ can be recognized by comparing the difference between the mapping patterns of Co and P elements. The regions where Co element is present but P element absent correspond to the locations of Co(OH)$_2$, as selectively marked by the dashed circles in the Co mapping pattern. The distribution of Co(OH)$_2$ derived from the mapping patterns is consistent with the result from the HRTEM images. On the basis of all these structural characterizations above, the structure of the CoPi/Co(OH)$_2$-Ta$_3$N$_5$ photoanode studied here can be illustrated in Figure 3.

The PEC water splitting activities of the Ta$_3$N$_5$ photoanodes with different co-catalysts were tested in a three electrode system and details were described in the
The bare Ta₃N₅ photoanode only delivered a photocurrent density of 0.25 mA cm⁻² at 1.23 V (vs. RHE), and this value rapidly decayed to almost zero within only 400s (Figure 4). The photocurrent density at 1.23 V (vs. RHE) was improved to 1.7 mA cm⁻² for the CoPi-Ta₃N₅ photoanode and an even higher value of 3.4 mA cm⁻² was obtained with the Co(OH)₂-Ta₃N₅ photoanode. The greatly enhanced photocurrent density indicates that the photo-holes are effectively extracted from Ta₃N₅ light absorber to surface co-catalysts. The higher value achieved with Co(OH)₂ co-catalyst means that Co(OH)₂ has a higher photo-hole extraction ability compared with CoPi, which is in accordance with the previous report. Despite of its higher activity, the Co(OH)₂-Ta₃N₅ photoanode exhibits a much faster photocurrent decay than the CoPi-Ta₃N₅ photoanode largely because of the poor ability of the non-continuous coating of Co(OH)₂ nanoparticles on the Ta₃N₅ nanorods in preventing the direct contact of water with Ta₃N₅. On the other hand, since the OER activity of CoPi is higher than that of Co(OH)₂, the photocurrent onset potential of the CoPi-Ta₃N₅ photoanode was more negative than that of the Co(OH)₂-Ta₃N₅ photoanode (797 mV vs 829 mV). What’s more interesting is that the onset potential was further negatively shifted by 27 mV in the CoPi/Co(OH)₂-Ta₃N₅ photoanode (Figure S3). This clearly indicates that the synergistic effect of CoPi and Co(OH)₂ in enhancing OER activity. Comparison of the OER activities of the CoPi-Ta₃N₅ and CoPi/Co(OH)₂-Ta₃N₅ electrodes evaluated in dark in the same electrolyte (Figure S4) shows a more negative OER current onset potential of the latter, which doubly confirms the synergistic effect of two co-catalysts. As a consequence of both the enhanced OER activity and water proof capacity of the
continuous shell consisting of CoPi and Co(OH)\textsubscript{2} dual co-catalysts, the CoPi/Co(OH)\textsubscript{2}-Ta\textsubscript{3}N\textsubscript{5} photoanode has a highest photocurrent density of 3.8 mA cm\textsuperscript{-2} among all four photoanodes studied here and displays the high stability with less 10% photocurrent decay in a 20 min test duration. It’s worth noting that there is an obvious oxidation peak in the J-V curve recorded on the Co(OH)\textsubscript{2}-Ta\textsubscript{3}N\textsubscript{5} photoanode, and the appearance of this oxidation peak results from the oxidation of Co(OH)\textsubscript{2} into CoOOH induced by photo-holes. It has been recognized that the Co(OH)\textsubscript{2}/CoOOH redox potential (~0.65V vs. RHE) is much negative compared to the OER potential (1.23 V vs. RHE).[33] However, the redox couple potential of Co\textsuperscript{2+}/Co\textsuperscript{3+} in CoPi is ~1.1 V vs. RHE,[34] approaching to the OER potential, which is hardly oxidized and its corresponding oxidation-current peak is easily submerged in the photocurrent. Consequently, the oxidation-current peaks are absent in the J-V curves recorded on the CoPi-Ta\textsubscript{3}N\textsubscript{5} and CoPi/Co(OH)\textsubscript{2}-Ta\textsubscript{3}N\textsubscript{5} photoanodes.

**Figure 4.** (a) J-V curves of bare Ta\textsubscript{3}N\textsubscript{5}, CoPi-Ta\textsubscript{3}N\textsubscript{5}, Co(OH)\textsubscript{2}-Ta\textsubscript{3}N\textsubscript{5} and CoPi/Co(OH)\textsubscript{2}-Ta\textsubscript{3}N\textsubscript{5} photoanodes tested under 1 sun simulator irradiation. (b) Time dependent photocurrent density at a fixed potential of 1.23 V vs. RHE.
Figure 5. (a) Nyquist plots of the CoPi-Ta$_3$N$_5$, Co(OH)$_2$-Ta$_3$N$_5$ and CoPi/Co(OH)$_2$-Ta$_3$N$_5$ photoanodes tested under 1 sun simulator irradiation at a fixed potential of 1.23 V (vs. RHE). (b) Zoomed in Nyquist plots at high frequency range.

Electrochemical impedance spectra can provide important results to understand the carrier dynamics across the interfaces. Nyquist plots are commonly adopted to analyze the carrier interfacial transfer resistances in PEC cells,[31,32] and the number and diameter of the semi-arcs appearing in Nyquist plots indicate the number of existed interfaces and the carrier transfer resistances across different interfaces. In general, the smaller the diameter of a semi-arc is, the faster carrier transfer across the corresponding interface is. The Nyquist plots of three Ta$_3$N$_5$ photoanodes modified with co-catalysts were recorded under light illumination at a fix potential of 1.23 V (vs. RHE) (Figure 5). As the co-catalyst shell has been introduced in the photoanodes, two semi-arcs are commonly recorded in the Nyquist plots. They correspond to the carrier transfer across the Ta$_3$N$_5$/co-catalyst solid interface and co-catalyst/electrolyte (solid/liquid) interface. The small semi-arc at high frequency range reflects the information of carrier transfer across the Ta$_3$N$_5$/co-catalyst solid interface. To compare the carrier transfer resistance across the solid interface among different photoanodes, the high frequency range of the
Nyquist plots was zoomed in as shown in Figure 5b. The Co(OH)$_2$-Ta$_3$N$_5$ photoanode exhibits the smallest semi-arc at the high frequency range compared with the other two photoanodes. After fitting the Nyquist plots with a proper tandem equivalent circuit, the carrier transfer resistance across the Co(OH)$_2$-Ta$_3$N$_5$ interface is determined to be $\sim 2.27 \, \Omega$, which is much lower than that (7.80 $\Omega$) across the CoPi-Ta$_3$N$_5$ interface and that (8.11$\Omega$) across the CoPi/Co(OH)$_2$-Ta$_3$N$_5$ interface. In contrast, the second semi-arc at low frequency range, which accounts for the carrier transfer resistance across the co-catalysts/electrolyte interface, is the biggest for the Co(OH)$_2$-Ta$_3$N$_5$ photoanode (127.1$\Omega$) and followed by the CoPi-Ta$_3$N$_5$ (71.44$\Omega$) and CoPi/Co(OH)$_2$-Ta$_3$N$_5$ (60.25$\Omega$) photoanodes. This phenomenon means that the OER catalytic activity is the highest for CoPi/Co(OH)$_2$ and followed by CoPi and Co(OH)$_2$. The results derived from the electrochemical impedance spectra are in good agreement with the results from the J-V curves. The Nyquist plot fitted parameters by a tandem equivalent circuit (see the inset in Figure 5a) were summarized in Table S1.

![Figure 6](image.png)

**Figure 6.** (a) IPCE spectra of the CoPi-Ta$_3$N$_5$, Co(OH)$_2$-Ta$_3$N$_5$ and CoPi/Co(OH)$_2$-Ta$_3$N$_5$ photoanodes. (b) Comparison of the amounts of H$_2$ calculated from the quantity of electric charge flow through the external circuit (black square) and H$_2$ generated in
the PEC cell (red circle).

The IPCE measurements were implemented to compare the wavelength dependent quantum efficiencies of the photoanodes. The curves of the quantum efficiency as a function of the wavelength of incident light for each photoanode in Figure 6a are similar to UV-visible absorption spectrum of the Ta₃N₅ matrix (Figure S5), suggesting that the photons absorbed at different wavelength regions can be utilized to excite valence band electrons for subsequent water splitting reaction. As the bandgap of Ta₃N₅ is ~2.1 eV, the photons with wavelength of <590 nm can be effectively absorbed and converted. The Co(OH)₂-Ta₃N₅ photoanode displays the higher quantum efficiencies in the whole responsive wavelength range as compared to the CoPi-Ta₃N₅ photoanode. Once the Co(OH)₂ was loaded on the CoPi-Ta₃N₅ photoanode, the resultant CoPi/Co(OH)₂-Ta₃N₅ photoanode exhibits the higher quantum efficiencies in the wavelength range from 425 to 560 nm in comparison with the Co(OH)₂-Ta₃N₅ photoanode. The obtained IPCE results are also consistent with the J-V measurements, where the CoPi/Co(OH)₂-Ta₃N₅ photoanode delivers the highest photocurrent density and the CoPi-Ta₃N₅ photoanode showed the lowest value. The relatively low quantum efficiencies in the region close to UV (400-420 nm) for the CoPi/Co(OH)₂-Ta₃N₅ photoanode may be caused by the co-catalyst shell that reduces light absorption of the Ta₃N₅ absorber. In addition, the Co(OH)₂-Ta₃N₅ photoanode delivers higher quantum efficiencies than two other photoanodes near the absorption edge range (550-600 nm), This abnormal phenomenon derives from the contribution of capacitive photocurrent from oxidizing
Co(OH)$_2$. As discussed on the J-V curves, Co(OH)$_2$ is easier to be oxidized into CoOOH by photo-holes from the Ta$_3$N$_5$ absorber compared to the water oxidation due to its more negative redox potential (~0.65 V vs, RHE), therefore, Co(OH)$_2$ has been frequently used as an promising material for supercapacitors.[35] The lower energetic photo-carriers induced by the long wavelength photons have the ability of oxidizing Co(OH)$_2$ and produce capacitive photocurrent, but they have a much lower capacity of oxidizing CoPi. So, it is believed that the higher IPCE of Co(OH)$_2$-Ta$_3$N$_5$ near the absorption edge range could result from the contribution of capacitive photocurrent from the oxidation of Co(OH)$_2$. The IPCE values of the CoPi/Co(OH)$_2$-Ta$_3$N$_5$ photoanode are higher than 30% before 540 nm. It is necessary to evaluate the Faraday efficiency of the efficient photoanode. The photocurrent produced by the CoPi/Co(OH)$_2$-Ta$_3$N$_5$ photoanode under one sun irradiation was recorded at a fixed potential of 1.23V (vs. RHE). To distinguish the effective current for water splitting from the recorded photocurrent, the amount of H$_2$ produced in the PEC test is compared with the theoretical amount of H$_2$ calculated from the recorded current in Figure 6b. The Faraday efficiency of the CoPi/Co(OH)$_2$-Ta$_3$N$_5$ photoanode is calculated to be higher than 90 %, indicating that most of the recorded photocurrent is associated with water splitting reaction.

**Conclusion**

By designing the shell consisting of a continuous CoPi layer at the bottom and many non-continuous Co(OH)$_2$ islands at the top of CoPi layer for the Ta$_3$N$_5$ nanorods, an efficient photoanode of CoPi/Co(OH)$_2$-Ta$_3$N$_5$ supported on Ta foil as the conductive
substrate for PEC water splitting is constructed. Owing to the remarkable functions of such a shell in segregating water from Ta$_3$N$_5$ to prevent self-oxidation of the nanorods and enhancing OER activity of co-catalysts together with the charge carrier separation, the constructed photoanode shows the greatly enhanced PEC water splitting performance in terms of activity and stability compared with three reference samples. The enhanced OER activity is largely attributed to the strong interaction between CoPi and Co(OH)$_2$ to create the boundaries associated active sites. At the bias of 1.23 V, the photoanode gives a photocurrent density of ~3.8 mAcm$^{-2}$ at 1.23 V (vs. RHE), and over 90% of the initial value can be retained after a 20 min stability test duration. The strategy shown here might be applicable to enhance the PEC performance of other light absorbers with wide absorption range but low resistance to self-oxidation.

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**Reference**


