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Cobalt phosphate modified TiO$_2$ nanowire arrays as co-catalyst for solar water splitting

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Abstract: The cobalt phosphate (Co-Pi) is photo-electrodeposited on the TiO$_2$ nanowire arrays in Co$^{2+}$ containing phosphate buffer. The resulting composite photoanode shows generally enhanced photocurrent near the flat band potential region, and represents 2.3 times photoconversion efficiency improvement compared to the pristine TiO$_2$ in neutral electrolyte. A negative effect on the photocurrent generation is also observed when loading TiO$_2$ with relatively thick Co-Pi layer, which is demonstrated to be due to the poor photohole transfer kinetics in the Co-Pi layer. Moreover, we find that the Co-Pi can facilitate the photoelectrochemical performance of TiO$_2$ over a wide range of pH value from 1-14. This improved activity is studies in detail by optical and electrochemical analysis. It is suggested that the overpotential demanding water oxidation reaction is changed into a facile pathway by the Co-based electro-catalyst. At the same time, the more significant band bending is induced by
the Co-Pi catalyst to decrease the charge recombination. This work provides a feasible route to reduce of the external power needed to drive water splitting by the coupling of electro-catalyst with photo-catalyst as well as important mechanism insights for other Co-Pi modified photoelectrodes for solar-driven water splitting.

**Introduction**

The photoelectrochemical (PEC) splitting of water into hydrogen and oxygen is a nice duplication of the nature photosynthesis which collects the energy of sunlight and stores it in the form of chemical bonds. TiO$_2$ is one of the most extensively studied semiconductor materials for solar water splitting due to its excellent chemical stability, non-toxicity and earth abundance.$^{[1-5]}$ Especially, the energy band position (-0.29 V vs. RHE of conduction band edge and 2.91 V vs. RHE of the valence band edge) endues TiO$_2$ with the latent capacity for full solar-driven water splitting.$^{[6, 7]}$ The water splitting process involves two complicated multi-electron half reactions ($2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^-$, $E^\theta=1.23$ V vs. RHE; $4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2$, $E^\theta=0$ V vs. RHE). Studies have indicated that the reactions between photogenerated holes and water molecules mainly limit the performance of PEC water splitting, as it generally occurs at a significant overpotential for the removal of a total of four electrons and four protons from two water molecules to form one O$_2$ molecule.$^{[9-10]}$ Therefore, even though the much more positive valence band edge of TiO$_2$ than the required potential for water oxidation thermodynamically, the water oxidation by photogenerated valence band holes is kinetically inefficient, and additional anodic bias are typically required before significant PEC water splitting is observed.$^{[11]}$ At the same time, the slow water oxidation reaction induces the large accumulation of photoholes at the electrode/electrolyte interface thus aggravates the electron-hole recombination and other side reactions.$^{[12]}$

Catalyst is a fine-tuned molecular machinery which can change the reaction mechanism thus reduce the reaction energy barrier to boost the chemical reaction rate.$^{[13, 14]}$ Integration of oxygen evolution electro-catalyst with a photon-absorbing substrate therefore is a promising approach to reduce the external power needed to
drive the catalyst’s electrolysis chemistry and improve the overall solar conversion efficiency. Considerable efforts have been devoted to develop suitable water oxidation electro-catalyst for photoelectrode.\textsuperscript{15-21} Recently, the amorphous cobalt-phosphate (Co-Pi) emerges to be an attractive candidate catalyst material.\textsuperscript{21-25} Compared to the precious metal (Ru, Ir) or metal oxide (RuO\textsubscript{2}, IrO\textsubscript{x}), extreme pH conditions required spinel and perovskite metal oxides oxygen evolution catalyst, Co-Pi possesses much advantages such as its earth abundant reserve, self-healing feature,\textsuperscript{26} and functionality under benign conditions.\textsuperscript{27} This active catalyst is believed to have a cubane structure resembling the oxygen-evolving complex of photosystem II.\textsuperscript{28} Many semiconductor materials have been coupled with the Co-Pi electro-catalyst to exploit its merit of as co-catalyst.\textsuperscript{29-33} For example, Steinmiller et al. reported that the Co-Pi modified ZnO photoanode shown improved PEC behavior with negatively shifted photocurrent onset potential and generally enhanced anodic photocurrent in the whole bias range.\textsuperscript{34} Unfortunately, the Co-Pi does not always represents the enhancement effect on PEC performance of light-absorption substrates. For example, Bledowski reported the Co-Pi decorated TiO\textsubscript{2}-C\textsubscript{3}N\textsubscript{4} for PEC water splitting, the photocurrent enhancement of which was limited only in a certain bias range.\textsuperscript{35} And the catalyst amount dependent PEC performance of the Co-Pi modified W-doped BiVO\textsubscript{4} was found in the report of Ye et al.\textsuperscript{36}

Therefore, for the better utilization of the positive catalytic effect of the Co-Pi for semiconductor photoanode, the certainty about the microscopic identity of the catalyst appears to be significantly in request. While several reports\textsuperscript{37-40} have confronted this issue, a generally acceptable nature interpretation of the Co-Pi electro-catalyst on photoanode substrate is far from satisfaction. For example, the creation of interface states by the Co-Pi deposition was introduced to explain the inconsistent catalytic effect of the Co-Pi on WO\textsubscript{3} when the applied bias varied form near flat band potential to more positive bias.\textsuperscript{37} However, Zhong et al. identified an O\textsubscript{2} evolution kinetic limitation of the Co-Pi catalyst, which would be largely overcome by more sparse deposition of Co-Pi on photoanode.\textsuperscript{38} A similar results of a related catalysts modified Fe\textsubscript{2}O\textsubscript{3} also was reported that the amount reduction of Ni(OH)\textsubscript{2} catalyst would
surmount the negative catalytic effect, while the slow formation of the active catalytic species (Ni^{4+}) was demonstrated to explain the catalytic mechanism.\textsuperscript{41} In contrast, Klahr et al. reported continual PEC improvement with increasing Co-Pi thickness on Fe\textsubscript{2}O\textsubscript{3}.\textsuperscript{39} Additionally, another study indicated that Co-Pi did not directly participate in water-oxidation reaction but instead played an indirect role by inducing additional band bending for photoanode semiconductor to reduce electron-hole recombination.\textsuperscript{42}

In this work, we report the co-catalytic effect as well as the mechanism insights of the Co-Pi electro-catalyst modified TiO\textsubscript{2} nanowire array photoanode. It is found that the anodic photocurrent of the TiO\textsubscript{2} electrode is generally improved by a sparse Co-Pi catalyst loading with its effect more pronounced when the band bending is less significant, and the solar-to-hydrogen conversion efficiency is enhanced by 2.3 times compared to its parent TiO\textsubscript{2} photoanode. A negative effect on the photocurrent generation is also observed when loading TiO\textsubscript{2} with thick Co-Pi catalyst, which is proposed to be due to the poor hole transfer kinetics of the Co-Pi layer. Finally, we demonstrate that the Co-Pi can facilitate the photoelectrochemical performance of TiO\textsubscript{2} over a wide range of pH value from 1-14. Based on a detailed electrochemical analysis and the predecessors’ initiations, a plausible interpretation of the co-catalytic mechanism is proposed. This work provides a feasible route for the solar energy conversion efficiency improvement by coupling of the electro-catalyst with photocatalyst as well as important mechanism insights for other Co-Pi modified photoelectrodes for solar water oxidation.

**Results and discussion**
Fig. 1. SEM images of (a) pristine TiO$_2$, and the TiO$_2$ with (b) 10 uC cm$^{-2}$ Co-Pi deposition and (c) 1 mC cm$^{-2}$ Co-Pi deposition. (d) EDS spectra collected from TiO$_2$/Co-Pi (1 mC cm$^{-2}$) sample.

The TiO$_2$ nanowire array electrodes used in this work were grown on fluorine-doped tin oxide glass (FTO) substrates by hydrothermal method reported elsewhere (methods, see supporting information). The TiO$_2$ nanowires are tetragonal in shape with diameter of ~75 nm (Fig. 1a). Co-Pi catalyst was decorated on the TiO$_2$ by photo-assisted electrodeposition in Co$^{2+}$ containing phosphate buffer with the amount controlled by varying the quantity of electric charge passed through the external circuit. The white TiO$_2$ electrode becomes slightly dark green after 10 mC cm$^{-2}$ Co-Pi deposition (see the inset in Fig. S1). Fig. 1b and Fig. 1c show the scanning electron microscope (SEM) images of the TiO$_2$ after the 10 uC cm$^{-2}$ and 1 mC cm$^{-2}$
Co-Pi deposition respectively, which show no apparent morphology change compared to the pristine TiO$_2$ nanowire arrays but the images becomes somewhat brighter, suggesting that the catalysts make the surfaces more insulating and hence more susceptible to charging effects from the electron beam. Although the catalyst can not be resolved by the SEM measurement, the existences of Co and P element are confirmed by the energy dispersive spectroscopy (Fig. 1d). X-ray diffraction (XRD) spectra reveal the rutile crystal phase of the TiO$_2$ nanowire array (Fig. S2). The absence of (110) peak at 2\(\theta\) of 27.4 indicates the vertically standing morphology of the nanowires, in consistent with the SEM observation. The indistinguishable XRD spectra of TiO$_2$/Co-Pi with pristine TiO$_2$ indicate the amorphous microstructure of Co-Pi catalyst. The UV-vis spectra of TiO$_2$ and TiO$_2$/Co-Pi show similar light absorption features, implying no additional band gap transition absorption induced by Co-Pi catalyst (Fig. S3). However, the Co-Pi catalyst layer may consume the incident light by nonproductive absorption, thus all the PEC test under light were carried out by backside illumination (from FTO to TiO$_2$) method.

![Graphs showing Ti 2p, O 1s, P 2p, and Co 2p binding energies](image-url)
Fig. 2. High resolution XPS spectra of TiO$_2$/Co-Pi composite electrode: (a) Ti 2p, (b) O 1s, (c) P 2p, (d) Co 2p. The black curve is the experimental result. The red curve is the summation of the synthetic peaks in color curves.

The surface composition and elemental chemical state of the TiO$_2$/Co-Pi composite electrode were examined by X-ray photoelectron spectroscopy (XPS) as shown in Fig. 2. The strong Ti 2p$_{3/2}$ and 2p$_{1/2}$ XPS peaks at about 458.68 and 464.48 eV are attributed to Ti$^{4+}$. The O 1s XPS spectra show a strong peak at \(~529.98\) eV and a shoulder peak at \(~531.48\) eV, which implies there are at least two kinds of O chemical states, including the crystal lattice oxygen (O$_L$) and hydroxyl oxygen (O$_H$) with increasing binding energy. The binding energy of P 2p is at \(~133.28\) eV, which is characteristic of P in the phosphate group, confirming that P exists as the form of PO$_4^{3-}$. The characteristic peaks of Co 2p$_{3/2}$ and Co 2p$_{1/2}$ at around 781.08 and 797.28 eV is in the typical range of Co$^{2+}$ and Co$^{3+}$ respectively. The main Co 2p$_{1/2}$ peak of Co$^{3+}$ ions generally appears between 794.0 and 794.7 eV, and the shift of this peak to a higher binding energy is indicative of an increase in the Co$^{2+}$/Co$^{3+}$ ratio in the sample. We believe that the Co$^{2+}$/Co$^{3+}$ ratio in the as-deposited Co-Pi catalyst is not as important as the total amount or nucleation density of the Co-Pi catalyst in affecting the overall catalytic ability, because the oxidation states of Co ions in the catalyst are supposed to continuously change in a cyclic manner (Co$^{2+/3+} \rightarrow$Co$^{4+} \rightarrow$Co$^{2+/3+}$) during the course of water oxidation.
Fig. 3. PEC measurements of the TiO$_2$ and the parent TiO$_2$ with 10 uC cm$^{-2}$ Co-Pi composite electrode in 0.1 M potassium phosphate electrolyte (pH=7). (a) Linear sweep voltammograms ($i$-$v$ curves) under constant 1 sun illumination at scan rate of 25 mV s$^{-1}$, (b) calculated photoconversion efficiencies, (c) transient photocurrent densities measured at 0 V and 0.4 V vs. Ag/AgCl with chopped light illumination.

Fig. 3 compares the PEC properties of pristine TiO$_2$ and the same TiO$_2$ coated with 10 uC cm$^{-2}$ Co-Pi catalyst measured in 0.1 M potassium phosphate electrolyte (pH=7). In Fig. 3a, the photocurrent of TiO$_2$ electrode is largely enhanced after the deposition of Co-Pi catalyst especially when the band bending is less significant. The
Mott-Schottky plots show that the pristine TiO$_2$ and composite TiO$_2$/Co-Pi electrodes have comparable flat band potentials under a certain frequency (Fig. S4). And no additional optical absorption by Co-Pi layer makes contribution to the enhanced photocurrent as evidenced by UV-vis spectra (Fig. S3) and the $i$-$V$ curves of FTO/Co-Pi electrode (Fig. S5). Therefore, the observed photocurrent improvement can be attributed to the reduced electron-hole recombination rate near the flat band potential caused by Co-Pi catalytic effect.$^{34,37}$ It is noteworthy that the catalytic effect for improving the photocurrent becomes less pronounced when the applied bias becomes more positive. This is because the increasing external bias can provide more powerful force to drive the electron-hole pair separation and water oxidation reaction even without the assistance of the electro-catalyst. In addition, we can observe that the photocurrent of TiO$_2$/Co-Pi electrode becomes even lower than that of the pristine TiO$_2$ when the external bias exceeds $\sim$1.6 V vs. RHE. This critical potential shifts to a more negative value when coating TiO$_2$ with increased amount of Co-Pi catalyst, which is ascribed to the slow hole transfer kinetics in Co-Pi catalyst and will be discussed later.

Compared to the negative role of Co-Pi catalyst in enhancing the photoactivity of TiO$_2$ in high bias region, the photocurrent enhancement in low bias region is more attractive since the high photocurrent at small bias potential can reduce the external power needed to drive water splitting and, thus, increases the overall efficiency of PEC hydrogen generation. The photoconversion (i.e., photon-to-hydrogen) efficiencies ($\eta$) of the TiO$_2$ and TiO$_2$/Co-Pi photoanodes are deduced from Fig. 3a using the following equation:$^{47}$

$$\eta = \frac{I(E_{\text{rev}}^\theta - V)}{J_{\text{light}}}$$

where $I$ is the photocurrent density ($\text{mA cm}^{-2}$) at the measured bias, $E_{\text{rev}}^\theta$ is the standard reversible potential which is 1.23 V vs. RHE for the water-splitting reaction at pH 0, and $V$ is the applied bias potential vs. RHE. $J_{\text{light}}$ is the irradiance intensity ($100 \text{ mW cm}^{-2}$). Fig. 3b presents the plots of the photoconversion efficiencies as a function of the applied bias. The pristine TiO$_2$ sample exhibits an optimal conversion efficiency of 0.075% at $\sim$0.9 V vs. RHE. Significantly, TiO$_2$/Co-Pi photoanode
achieves the highest efficiency of 0.17 % at a relatively low bias of ~0.7 V vs. RHE. The more than 2 times photoconversion efficiency enhancement at smaller external bias directly demonstrates the coupling of Co-Pi with TiO₂ is an available way for higher PEC behavior of TiO₂.

Fig. 3c displays the transient photocurrent curves (i-t curves) collected under chopped light illumination. At -0.2 V vs. Ag/AgCl, the TiO₂/Co-Pi and the pristine TiO₂ photoanodes both show spikes within the first second of irradiation. These spikes can be attributed to the charge carrier accumulation at the electrode-electrolyte interface due to the slow oxygen evolution kinetics or oxidization of trap states on the surface and in the bulk by charge carriers. However, the steady-state photocurrent density of TiO₂/Co-Co-Pi photoanode is retained 6 times more than that of the parent TiO₂ photoanode, which is ascribed to the relieved charge accumulation and boosted water oxidation reaction due to the Co-Pi catalyst. When the applied bias is 0.4 V vs. Ag/AgCl, the difference between photocurrent generated from the TiO₂/Co-Pi and bare TiO₂ is reduced, which is in accordance with the results in Fig. 3a. While spikes are still exhibited by the pristine TiO₂ upon illumination, only negligible reduction can be identified by TiO₂/Co-Pi electrode. The slight decrease of the initial photocurrent can be partially attributed to cobalt oxidation, which is an essential step in the catalytic water oxidation mechanism.

Fig. 4. i-v curves of TiO₂ coated with different amount of Co-Pi catalyst measured in 0.1 M potassium phosphate electrolyte (pH=7) under constant 1 sun illumination at scant rate of 25 mV s⁻¹.
As mentioned above, a negative effect on photocurrent generation may be induced by Co-Pi catalyst in high bias region especially when the Co-Pi layer is thick. Fig. 4 shows the $i$-$v$ curves of the TiO$_2$ nanowire array electrode and the same TiO$_2$ coated with different amount of Co-Pi catalyst. The red line is for the TiO$_2$/Co-Pi with 10 uC cm$^{-2}$ (referred as TiO$_2$/Co-Pi-s, small) and the orange line is for the one with 1 mC cm$^{-2}$ (referred as TiO$_2$/Co-Pi-l, large) passed through the external bias during deposition. Obviously, the photocurrent plateau of TiO$_2$/Co-Pi-l is depressed at a relatively low level compared to that of parent TiO$_2$ and TiO$_2$/Co-Pi-s, with the photocurrent improvement restricted in the range of 0.2-0.95 V vs. RHE. Not like the TiO$_2$/Co-Pi-s, the anodic scanning photocurrents of TiO$_2$/Co-Pi-l show strong scan rate dependence in the cyclic voltammograms (Fig. S6). This result implies that assignable photocurrent enhancement of TiO$_2$/Co-Pi-l is coming from the charging effect, where the TiO$_2$/Co-Pi-l electrode functioned as a pseudocapacitor electrode. A similar Co-Pi thickness dependence of the photocurrent has also been observed previously in Fe$_2$O$_3$/Co-Pi photoanode.\cite{38} Based on the proposed catalytic mechanism that involves the Co$^{2+/3+} \rightarrow$ Co$^{4+} \rightarrow$Co$^{2+/3+}$ reaction circle by Surendranath et al.,\cite{49} a plausible explanation for negative influence on photocurrent generation caused by thick Co-Pi layer is given as following. The catalytic water oxidation reaction is happened at the Co/electrolyte interface. If the Co-Pi layer is extremely thin (e.g., only one layer Co$^{2+/3+}$ linked to the surface of TiO$_2$ by phosphate groups), the directly linked Co$^{2+/3+}$ on TiO$_2$ surface is easy to capture the photoholes to produce active catalytic species (Co$^{4+}$)\cite{50} for water oxidation. However, when the Co-Pi layer becomes thicker, the photoholes must be transferred to the Co-Pi/electrolyte interface through many in-between Co-Pi molecules. The slow hole transfer rate in the intermediate Co-Pi may be due to the thermodynamically difficult reaction between Co ions with adjacent valence (e.g., Co$^{4+}$ and Co$^{3+}$), which is responsible for the depressed photocurrent. As a result, the holes are accumulated at the TiO$_2$/Co-Pi interface and accelerate the electron-hole recombination in return.
The above PEC measurement results demonstrate the availability to obtain PEC performance improvement for TiO$_2$ in neutral electrolytes by a sparse Co-Pi decoration, further, we investigate this positive catalytic effect in acid and alkaline electrolytes. It should be mentioned that to keep the same ionic environment (e.g., ionic species, ionic strength) as far as possible, four equal 0.1 M potassium phosphate electrolytes were prepared and the pH value of them were accurately adjusted to 1, 4, 10, 14 respectively by concentrated H$_2$SO$_4$ or KOH aqueous solution. As shown in Fig. 5, the photocurrent densities of the parent TiO$_2$ nanowire array electrodes in different pH value electrolyte are all improved after the modification of Co-Pi catalyst in the low bias potential region. The photoconversion efficiencies (inset in each $i$-$v$ curve panel in Fig. 5) are improved by 1.98, 1.42, 1.92, 1.46 times more than that of
the corresponding parent TiO$_2$ electrode in pH 1, 4, 10 and 14 electrolytes, respectively. These results indicate that the Co-Pi catalyst can facilitate the PEC behavior of TiO$_2$ over a wide range of pH value from 1-14. The enhancement in wide range pH value implies the promising applications of Co-Pi modification for other light absorption substrates in various pH electrolyte.

Fig. 6. Schematic band diagrams illustrating the proposed catalytic mechanism of Co-Pi on TiO$_2$ for PEC water oxidation.

Fig. 6 illustrates the proposed explanation for the improved PEC performance of the TiO$_2$ after the Co-Pi modification. As the light absorption consideration has been excluded, the enhanced photocurrent can be mainly attributed to the reduced charge carrier recombination which is induced by several reasons. First, as an oxygen evolution catalyst, the Co-Pi can catalyze the water electrolysis process to proceed at a low overpotential by changing the reaction pathway.$^{51}$ When combined with the TiO$_2$, the Co-Pi use the valence band photohole of the TiO$_2$ to drive $\text{Co}^{2+/3+} \rightarrow \text{Co}^{4+} \rightarrow \text{Co}^{2+/3+}$ circular catalytic reactions, accompanied by the fast output of photohole from TiO$_2$ to water molecule (i.e., water oxidation) if the Co-Pi layer is thin enough. Thus, the relieved charge accumulation at the electrode/electrolyte decreases the electron-hole recombination rate and leads to enhanced overall PEC performance. Second, the additional band bending at the electrode/electrolyte interface may be created by the Co-Pi catalyst, which can also reduce the surface charge recombination.$^{52}$ In Fig. S4, the Mott-Schottky plot of TiO$_2$/Co-Pi exhibits a larger slope compared to that of the parent TiO$_2$ electrode, indicating the decreased donor density in TiO$_2$/Co-Pi.$^{53}$ The decreased donor density may be due to the
formation of TiO₂/Co-Pi heterojunction which depletes of electrons in the TiO₂ conduction band and results in the additional band bending.⁵⁴

**Summary**

We have studied the co-catalytic effect by coupling the Co-Pi oxygen evolution electro-catalyst with TiO₂ photocatalyst for solar water splitting. Electrochemical analyst demonstrates that the PEC performance of TiO₂ is substantially improved by relatively sparse Co-Pi modification especially in the low bias region. It is also observed that the increasing of the Co-Pi amount have negative effect on the photocurrent generation, which is demonstrated to be due to the poor photohole transfer kinetics in the Co-Pi layer. Moreover, we find that the Co-Pi can facilitate the PEC performance of TiO₂ over a wide range of pH value from 1-14. The enhanced PEC behaviors are benefited from the reduced change recombination caused by Co-Pi catalyst due to the changed water oxidation mechanism and enhanced band bending. This work provides a feasible route to reduce of the external power needed to drive water splitting by the coupling of electro-catalyst with photocatalyst as well as important mechanism insights for other Co-Pi modified photoelectrodes for solar-driven water splitting.

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