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Supporting Information

ABSTRACT: Ta$_3$N$_5$ nanostructures are widely explored as anodes for photoelectrochemical (PEC) water splitting. Although the material shows excellent semiconductive properties for this purpose, the key challenge is its severe photocorrosion when used in typical aqueous environments. In the present work we introduce a NiFe layered double hydroxide (LDH) cocatalyst that dramatically reduces photocorrosion effects. To fabricate the Ta$_3$N$_5$ electrode, we use through-template anodization of Ta and obtain oxide nanorod arrays that then are converted to Ta$_3$N$_5$ by high temperature nitridation. After modification with our cocatalyst system, we obtained solar photocurrents of 6.3 mA cm$^{-2}$ at 1.23 V$_{RHE}$ in 1 M KOH, and an electrode maintains about 80% of the initial activity for extended irradiation times.

INTRODUCTION

Photoelectrochemical (PEC) water splitting offers the capability of harvesting the energy in solar radiation and transferring it directly into a chemical fuel in the form of hydrogen. To design a PEC system that optimally utilizes solar light, the appropriate choice of photoelectrode materials involves not only the “right” optical absorption properties and relative band edge positions to water but also chemical and photoelectrochemical stability in aqueous electrolytes. Metal oxides, such as Fe$_2$O$_3$, TiO$_2$, and BiVO$_4$, have received wide attention as photoelectrodes for PEC light conversion. However, either due to nonoptimized energetics or other intrinsic deficits such as very low carrier lifetime, these materials show theoretical and practical limits for an efficient use. Thus, considerable efforts have been focused on other semiconductor materials with more appropriate band positions and improved charge carrier transport properties.

Among the nonoxide semiconductors, (oxy) nitrides, namely, Ta$_3$N$_5$ and TaON, emerge as promising candidates for PEC overall water splitting. The (oxy) nitride materials are able to reduce and oxidize water in the presence of appropriate sacrificial reagents under visible-light irradiation. Also as a photoelectrode Ta$_3$N$_5$ has recently attracted intensive interest, because its maximum possible solar-to-hydrogen efficiency is as high as 15.9% under AM 1.5G irradiation. However, Ta$_3$N$_5$ is highly prone to photocorrosion in aqueous media. To solve the problem, efforts have been made on alleviating accumulation of photogenerated holes at the semiconductor surface by suitable cocatalysts that facilitate water oxidation. For example, Ta$_3$N$_5$ has been modified with classic O$_2$ evolution catalysts, such as IrO$_2$. Although this measure indeed slows down photocorrosion, still a strong photocurrent decay is observed with a decrease to ~20% of the initial photocurrent value after illumination for 20 min. The modification of
Ta₃N₅ with Co(OH)ₓ, another excellent water oxidation catalyst (WOC), can lead to a high photocurrent (up to 5.2 mA cm⁻² at 1.23 V_RHE), but the initially high photocurrent is maintained only for less than 10 min.²⁴,²⁵ Also CoOₓ decorated Ta₃N₅ electrodes were explored but still they show only about 30% of the initial photocurrent after 2 h irradiation.²⁶ Recently, Domen et al.²⁷ reported a continuous production of oxygen for 100 min on a cobalt phosphate (Co-Pi) WOC modified Ba–Ta₃N₅ photoanode at a moderate potential, 0.9 V_RHE. The photoanode was measured in an aqueous solution of 0.5 M K₂HPO₄ electrolyte at pH = 13.

Due to these findings it is clear that new and effective photocatalysts are needed not only in order to reduce the photocurrent-onset overpotential and enhance the overall energy conversion efficiency but also to extend the long-term stability of the nitride.

For this, one way considers mixed metal oxides of Fe, Co, and Ni that were reported to have a high oxygen evolution reaction (OER) activity as electrocatalysts in alkaline medium, often outperforming simple Co oxides and hydroxides.²⁸–³¹ Recently, a nickel–iron layered double hydroxide (NiFe-LDH)–carbon nanotube electrocatalyst was reported that provides a higher OER electrocatalytic activity and stability than commercial Ir-based catalysts in alkaline solutions.²⁸,³² The key features of this catalyst are ultrathin nanoplatelets of a highly OER-active NiFe-LDH structure.

In the present work, we introduce the use of such a crystalline NiFe-LDH film as a hole transfer catalyst on a Ta₃N₅ photoanode, which leads to an outstanding stability of the electrode against photocorrosion. The NiFe-LDH decorated Ta₃N₅ photoanode maintains about 90% of the initial activity after 2 h irradiation. Moreover, combined with Co(OH)ₓ and Co-Pi, the photoanode yields a photocurrent up to 6.3 mA cm⁻² at a potential of 1.23 V_RHE under AM 1.5G simulated sunlight (100 mW cm⁻²) and maintains about 80% of the initial activity after 2 h irradiation; this is, we believe, the highest long-term stable photocurrent of a Ta₃N₅ nanorod photoanode reported to date.

## EXPERIMENTAL SECTION

### Materials

All chemicals were analytical grade and were used as purchased without further purification. Solutions were prepared using high purity water purified with a Barnstead purification system (resistivity ≥ 18.2 MΩ).

### Fabrication of Ta₃N₅ Samples

Vertically aligned Ta₂O₅ nanorods were grown on a Ti foil with a thickness of 0.1 mm (99.9% purity, Advent, U.K.) by thermal–magnetization anodization.²²,³³ The Ta foils were cut into a diamond saw and then cleaned by sonication in acetone and ethanol. An Al layer with a thickness of ~1.3 µm was deposited on the Ta substrate by thermal evaporation (using a PLS 500 evaporator system). The Al layer was anodized in 0.3 M oxalic acid at 40 V for 0.5 h at room temperature under stirring, to form a porous anodic alumina (PAA) mask. Subsequently, the nanochannels of the PAA mask were widened by immersion into a 5% H₃PO₄ aqueous solution at 60 °C for 90 s, 3 min, and 4 min. The masked Ta substrates were then anodized in a 0.5 M H₂BO₃ aqueous solution at room temperature under stirring. The anodizing voltage was ramped from 0 to 600 V at a rate of 0.05 V s⁻¹ and held at 600 V for 1 h. The Ta₂O₅ nanorods embedded into the PAA mask were released by etching away the PAA mask with a 5% H₂PO₄ aqueous solution at 60 °C for 4 h. To obtain Ta₃N₅ nanorod arrays, the as-grown Ta₂O₅ nanorod arrays on the Ta foils were then heated in a quartz tube furnace in a gaseous atmosphere of NH₃ with a flow rate of about 200 mL min⁻¹ at 1000 °C for 2 h.

### Decoration of Co(OH)ₓ on Ta₃N₅ Nanorod Arrays

Before the water splitting measurement, Co(OH)ₓ and Co-Pi were deposited on the Ta₃N₅ nanorod arrays as oxygen evolution catalysts. For the Co(OH)ₓ decoration, the nanorod photoanodes were immersed in a mixed solution of 0.1 M CoSO₄ and 0.1 M NaOH with a ratio of 1:1 for 30 min and then washed with DI water and dried in N₂.

### Decoration of Co-Pi on Co(OH)ₓ/Ta₃N₅ Nanorod Arrays

Decoration of Co-Pi catalyst on the Co(OH)ₓ/Ta₃N₅ nanorod arrays was conducted by an electrodeposition method. For this the Co(OH)ₓ/Ta₃N₅ nanorod layers were held potentiostatically at 1.0 V versus Ag/AgCl for 8 min in a solution containing 0.5 mM Co(NO₃)₂ and 0.1 M KH₂PO₄ at pH = 7. Then the electrodes were washed with DI water and dried in N₂.

### Decoration of NiFe-LDH on Ta₃N₅ Nanorod Arrays

For the precursor solution, 186 mg of Ni(NO₃)₂·6H₂O and 51.6 mg of Fe(NO₃)₃·9H₂O were dissolved in 4.64 and 3.20 mL of DI water, respectively. The solution was dispersed in a mixture of 32 mL of N,N-dimethylformamide (DMF) and 60 mL of DI water, followed by sonication for 1 h. The Ta₃N₅ nanorod arrays were put in a 250 mL Teflon-lined autoclave filled with the precursor solution. The autoclave was then heated for the solvothermal reaction to 120 °C for 15 h, followed by another solvothermal treatment at 160 °C for 2 h. Then the electrodes were washed with DI water and dried in N₂.

### Decoration of NiFe-LDH on Co-Pi/Co(OH)ₓ/Ta₃N₅ Nanorod Arrays

To decorate the cocatalyst on the NiFe-LDH/Ta₃N₅ nanorod arrays, the samples were immersed in the mixed solution of 0.1 M CoSO₄ and 0.1 M NaOH for 30 min, followed by washing with DI water and drying in N₂. Finally, the electrodes were further modified with Co-Pi catalyst via electrodeposition method as described above (0.5 mM Co(NO₃)₂ and 0.1 M KH₂PO₄ at pH = 7 at 1 V versus Ag/AgCl for 8 min). The electrodes were washed with DI water and dried in N₂.

### Characterization

X-ray diffraction (X̅pert Philips MPD with a Panalytical X'Celerator detector, Germany) was carried out using graphite monochromized Cu Kα radiation (Wavelength 0.154056 nm). Chemical characterization was carried out by X-ray photoelectron spectroscopy (PHI 5600, spectrometer, U.S.A.) using Al Kα monochromated radiation. A field-emission scanning electron microscope (Hitachi FE-SEM S4800, Japan) was used for the morphological characterization of the electrodes. TEM electron microscopy was performed on a FEI Tecnai G2 20 S-TWIN with LaB₆-cathode, 200 kV accelerating voltage, and resolution limit 0.24 nm. The absorption of the samples was measured using a UV/vis spectrometer (Lambda 950) using integrating spectra.

### Photoelectrochemical and Electrochemical Measurements

The photoelectrochemical experiments were carried out under simulated AM 1.5G (100 mW cm⁻²) illumination provided by a solar simulator (300 W Xe with optical filter, Solarlight; RT). One M KOH aqueous solution was used as an electrolyte. A three-electrode configuration was used in the measurement, with the Ta₃N₅ electrode serving as the working electrode (photoanode), an Ag/AgCl (3 M KCl) as the reference electrode, and a platinum foil as the counter electrode. Photocurrent vs voltage (I–V) characteristics were recorded by scanning the potential from −0.3 to 0.8 V (vs Ag/AgCl (3 M KCl)) with a scan rate of 10 mV s⁻¹ using a Jaisle IMP 88 PC potentiostat. The measured potentials vs Ag/AgCl (3 M KCl) were converted to the reversible hydrogen electrode (RHE) scale using the relationship

$$E_{RHE} = E_{Ag/AgCl} + 0.059 \text{ pH} + E^{0}_{Ag/AgCl}$$

where $E^{0}_{Ag/AgCl}$ is the experimentally measured potential, and $E^{0}_{Ag/AgCl} = 0.209$ V at 25 °C for an Ag/AgCl electrode in 3 M KCl. The stability measurement for the Ta₃N₅ electrode was conducted at 0.23 V (vs Ag/AgCl (3 M KCl)) in 1 M KOH as a dependence of time. For all experiments at least three samples in the same condition were prepared and measured.

Photocurrent spectra were acquired at an applied potential of 0.23 V (vs Ag/AgCl (3 M KCl)) in 1 M KOH recorded with 20 nm steps in the range of 400–600 nm using an Oriel 6365 150 W Xe-lamp equipped with an Oriel Cornerstone 7400 1/8 m monochromator. The wavelength-dependent incident photon-to-current efficiency (IPCE) was calculated according to the following equation:

$$IPCE = \frac{I_{ph}}{P_{incident} \cdot \alpha}$$
where \( i_{ph} \) is the photocurrent (mA), \( \lambda \) is the wavelength (nm) of incident radiation, and \( p_{in} \) is intensity of the incident light irradiating on the semiconductor electrode at the selected wavelength (in mW).

Electrochemical impedance spectroscopy (EIS) was performed by using of Zahner IM6 (Zahner Elektrik, Kronach, Germany). Measurements were performed by applying 1.23 \( V_{\text{RHE}} \) at a frequency range of 100 000 to 0.1 Hz with an amplitude of 10 mV. Cyclic voltammetry (CV) was performed with 3 cycles at a scan rate of 5, 20, 50, and 100 mV \( s^{-1} \), respectively, under light and dark conditions. Mott–Schottky analysis was carried out in a DC potential range 0–1.7 \( V_{\text{RHE}} \) with a frequency of 1 Hz under dark conditions. All the impedance and CV measurements were carried out in 1 M KOH solution using Schott KL1500 electronic light source (Halogen lamp 15 V, 150 W).

**Faradaic Efficiency.** A two-electrode cell was used to measure the Faradaic efficiency. A Ta$_3$N$_5$ nanorod photoanode and a Pt foil were used as a working electrode and a counter electrode, respectively. The Ta$_3$N$_5$ nanorod photoelectrodes were biased at 1.23 \( V_{\text{RHE}} \) in a 1 M KOH solution using of Zahner IM6 (Zahner Elektrik, Kronach, Germany). Impedance and CV measurements were carried out in 1 M KOH using Schott KL1500 electronic light source (Halogen lamp 15 V, 150 W).

\[
\text{IPCE (%)} = \left( \frac{1240 \times i_{ph}}{\lambda \times p_{in}} \right) \times 100
\]

Figure 1a–d illustrates the fabrication steps of the nanorod geometry using a through-mask-anodization approach. First we evaporated an aluminum layer on a Ta substrate. The Al layer was then anodized to form ordered porous alumina as described in the Experimental Section. In a second anodization step, the Ta substrate was oxidized through the porous alumina mask under a high electric field forming Ta$_2$O$_5$ nanorods in a H$_2$BO$_3$ electrolyte. For adjusting the Ta$_2$O$_5$ nanorod diameter, pore-widening of the PAA was carried out using H$_3$PO$_4$ with a part of the specimens (that is, they were subjected to open-circuit dissolution before the second anodizing step). Due to the nature of the through-hole anodization process, the anodic Ta-oxide films formed are composed of an upper layer of tantala nanocolumns penetrating into the alumina pores and a lower layer of continuous tantalum oxide underneath the alumina film. Figure 1e–h shows SEM images of the ordered Ta$_2$O$_5$ nanorod arrays on the compact oxide layer. Clearly, a continuous densely packed tantalum oxide nanorod layer, in this case with a thickness of 330 nm, is obtained. The mean diameter of the columns is approximately 110 nm, which is apparently larger than that of the pores in the overlying alumina film (Supporting Information Figure S1c). Underneath the nanorod array, an \( \sim 750 \) nm thick oxide layer is observed (Figure 1g). Supporting Information Figures S1 and S2 show the effect of pore widening on the growth of nanorod arrays and the underneath oxide layers. The diameter and thickness of the columns change from 60 to 110 nm and 490 to 330 nm, respectively, when increasing the pore-widening time from 90 s to 4 min. The ratio between the nanorod array and compact oxide layer is decreased from 1:1 to 1:2, as the open pore-widening time is increased from 90 s to 4 min (Supporting Information Figure S2). This is similar to the results originally reported by Takahashi et al., who ascribed this effect to the dielectric properties of the films formed by reanodizing through the widened pores. It is noteworthy that the pore widening leads not only to a morphology change but also to a change in the chemical composition of anodic tantala layers.

Figure 2a and Supporting Information Figure S3 show SEM images of the Ta$_3$N$_5$ nanorod arrays after nitriding at 1000°C for 2 h. The diameter and thickness of Ta$_3$N$_5$ columns decrease to \(~100\) nm and \(~250\) nm, respectively, due to the volume decrease when Ta$_2$O$_5$ is converted to Ta$_3$N$_5$. The base oxide layer underneath the nanorod arrays changes to a mesoporous nanoparticle layer (Figure 2a). X-ray diffraction (XRD) patterns (Figure 3a) show the presence of peaks that can be...
assigned to Ta$_2$N and Ta$_5$N phases. The Ta$_5$N phase is formed by nitridation of the interlayer that was originally formed during the through-mask anodization step. In Domen et al.'s work, barium (Ba) doping of the Ta$_3$N$_5$ electrodes drastically changed the property of the oxide layer between the nanorod array and Ta substrate. The nondoped oxide layer was reported to contain Ta$_2$N and Ta$_5$N; due to the Ta$_5$N$_6$ compound it was described to be much more resistive than a Ba doped layer, which contained only Ta$_2$N. Thus, the activity of the nanorod photoanode could be improved if Ta$_5$N$_6$ phase formation was suppressed. However, in our work, only the Ta$_5$N phase was observed for the undoped electrode, which was achieved by using a high NH$_3$ flow rate (200 sccm). In our case, the presence of only the Ta$_2$N subnitride phase provides already a high electrical conductivity that aids the electron transfer from the nanorods/porous layers to the Ta substrate.

Supporting Information Figure S4a,b shows the SEM images of a Ta$_3$N$_5$ electrode after NiFe-LDH deposition using the hydrothermal method. The nanoplatelet size of NiFe-LDH is typically ~400 nm (Figure 2d) and appears as nearly transparent patches on the top surface of the Ta$_3$N$_5$ electrodes (Supporting Information Figures S4b and S5). The thickness of the nanoplatelets was estimated to be 10–20 nm (Figure 2f). The XRD pattern of the as-prepared NiFe-LDH (Supporting Information Figure S6) is consistent with the typical profile of LDH materials. X-ray photoelectron spectroscopy (XPS) corroborated the existence of both Ni and Fe in the hybrid material, as apparent from the high-resolution Ni 2p and Fe 2p spectra (Figure 3b,c). The O 1s spectrum (Figure 3d) is fitted with two peaks at 531.9 and 529.4 eV, which are corresponding to hydroxyl and oxide species, respectively. The absence of the Ta 4p peak in XPS (Figure 3e) is in line with almost a full coverage of Ta$_3$N$_5$ with the NiFe-LDH compared with the bare Ta$_3$N$_5$ (Supporting Information Figure S7).

In order to improve the PEC water splitting and to shift the photocurrent onset potential to lower values, additionally Co(OH)$_x$ combined with Co-Pi was employed as cocatalyst. Co(OH)$_x$ nanoparticles were deposited on the Ta$_3$N$_5$ nanorod arrays by an immersion method (see Experimental Section). After completion of a homogeneous Co(OH)$_x$ decoration, a thin layer of Co-Pi nanoparticles was additionally deposited on the Co(OH)$_x$/Ta$_3$N$_5$ nanorod surface by electrodeposition, resulting in the formation of Co-Pi+Co(OH)$_x$/Ta$_3$N$_5$ nanorod arrays. The optimum amount of Co-Pi nanoparticles for efficient water splitting can be adjusted by controlling the electrodeposition time (Supporting Information Figure S8a). Figure 4 provides the current–potential curves of the electrodes under AM 1.5G conditions in 1 M KOH electrolyte.

For the Ta$_3$N$_5$ photoanode (Figure 4a), a considerable increase in dark current density occurs at ~0.9 VRHE and the photocurrent increases to 1.7 mA cm$^{-2}$ at 1.23 VRHE (Figure 4d). The photocurrent density of Co-Pi+Co(OH)$_x$/Ta$_3$N$_5$ x nanorods is increased about 7-fold at a potential of 1.23 VRHE in the KOH electrolyte.
arrays. The low onset potential and high photocurrent density reflect a clearly higher photoconversion efficiency for the Co-Pi +Co(OH)/NiFe-LDH/Ta3N5 electrode.

We also considered the effect of nanorod/underlayer dimensions on the PEC water splitting performance using Co(OH)/Ta3N5 and Co-Pi+Co(OH)/Ta3N5 electrodes, as shown in Supporting Information Figure S9a. The photoanode with large diameter rods (~110 nm) and a thick oxide layer underneath (~750 nm) yields a photocurrent density of 4.1 mA cm⁻² at 1.23 V_RHE, which is two times higher than for photoanodes with diameters of 60 and 90 nm, i.e., also corresponding to a smaller thickness of the entire oxide layer. The increase in PEC activity with large diameter nanorod arrays can mainly be ascribed to the increased porosity of the porous layer and less defective nanorods.

Overall, above-reported magnitudes of the photocurrent density are among the best ever reported for Ta3N5, and even more significant effects observed in this work is the use of the NiFe system to induce a high photocorrosion stability. Figure 5 shows photocurrent versus time of Ta3N5, NiFe-LDH/Ta3N5, Co-Pi+Co(OH)/Ta3N5, and Co-Pi+Co(OH)/NiFe-LDH/Ta3N5, and Co-Pi+Co(OH)/NiFe-LDH/Ta3N5 electrochemical impedance spectroscopy (EIS) measurements were carried out covering the frequency range of 10⁰–0.1 Hz and using an amplitude of 10 mV as shown in Figure 6a. The results were fitted using the equivalent circuit,²¹,³⁴ shown in Figure 6b, in which R_s represents the solution resistance and the capacitance C_C is a resistance R_C, which characterize the charge transfer behavior across the electrode-solution interface.

In order to explore the interfacial properties between the electrodes and the electrolyte, the capacitance of nanorod/underlayer dimensions on the PEC water splitting performance using Co(OH)/Ta3N5 electrode rapidly decays to a negligible level within minutes as the surface is oxidized. This can be ascribed to photocorrosion and some extent of dark corrosion (as widely reported in literature²⁰–²³). Photocorrosion is caused by an accumulation of photogenerated holes at the surface of Ta3N5. This, in turn, is due to the hole transfer kinetics from the semiconductor valence band to water. If Co(OH)_2 and Co-Pi as cocatalysts are decorated on the Ta3N5 photoanode, a substantial enhancement in photoactivity is achieved compared to the bare Ta3N5 electrode. However, the photocorrosion of Co-Pi+Co(OH)/Ta3N5 electrode is still poor, in that only about 20% of the initial photocurrent remains at 2 h irradiation. The declining photocurrent trend is similar to that of IrO2 modified Ta3N5.²² In contrast, the NiFe-LDH/Ta3N5 electrode retains about 90% of the initial value even after 2 h of irradiation. The photocurrent increases, partially at the beginning stage, which is attributed to a "surface charging" process. This phenomenon indicates that surface-reaching holes are initially stored, which in turn increases a recombination flux of electrons at the surface.²⁶ XPS analysis after the stability test in Supporting Information Figure S10 shows a weak Ta 4p peak, and some cracks are also formed on the electrode surface during the PEC water splitting, evident in SEM as shown in Supporting Information Figure S4c. Thus, the slight deactivation might be associated with partial exposure of Ta3N5 to the electrolyte caused by these cracks. However, for the cobalt cocatalysts decorated NiFe-LDH/Ta3N5 electrode, the activity only mildly decreases in the initial 15 min but then exhibits a steady photocurrent of ~5 mA cm⁻² (about 80% of the initial activity) reliably for at least 2 h of irradiation. (Results for longer exposure times become less reliable and vary from sample to sample, which may reflect the finding that crack formation and pinholes in the cocatalyst layer may allow electrolyte penetration and thus a slow corrosion of the nitride phase.) Nevertheless, the results indicate that the NiFe-LDH layer efficiently prevents photocorrosion, restrains the recombination pathways, and improves the kinetic transport of photogenerated charge carriers away from the Ta3N5 surface. The observed photostability of Ta3N5 based systems at this high level of a photocurrent density (~5 mA cm⁻²) for several hours has not been achieved for any Ta3N5 nanorod arrays.

In order to explore the interfacial properties between the electrodes and the electrolyte, electrochemical impedance spectroscopy (EIS) measurements were carried out covering the frequency range of 10⁰–0.1 Hz and using an amplitude of 10 mV as shown in Figure 6a. The results were fitted using the equivalent circuit,²¹,³⁴ shown in Figure 6b, in which R_s represents the solution resistance and the capacitance C_C, and a resistance R_C, which characterize the charge transfer behavior across the electrode-solution interface.

Figure 5. Steady-state photocurrents of the bare Ta3N5 (black curve), NiFe-LDH/Ta3N5 (green curve), Co-Pi+Co(OH)/Ta3N5 (red curve), and Co-Pi+Co(OH)/NiFe-LDH/Ta3N5 (blue curve) nanorod arrays measured in 1 M KOH solution at 1.23 V_RHE under AM 1.5G simulated sunlight (100 mW cm⁻²).

Figure 6. (a) Electrochemical impedance spectra of the bare Ta3N5, NiFe-LDH/Ta3N5, Co-Pi+Co(OH)/Ta3N5, and Co-Pi+Co(OH)/NiFe-LDH/Ta3N5 electrodes for continuous illumination under AM 1.5G simulated sunlight at 1.23 V_RHE for extended times. The photocurrent of the bare Ta3N5 electrode rapidly decays to a negligible level within minutes as the surface is oxidized. This can be ascribed to photocorrosion and some extent of dark corrosion (as widely reported in literature²⁰–²³). Photocorrosion is caused by an accumulation of photogenerated holes at the surface of Ta3N5. This, in turn, is due to the hole transfer kinetics from the semiconductor valence band to water. If Co(OH)_2 and Co-Pi as cocatalysts are decorated on the Ta3N5 photoanode, a substantial enhancement in photoactivity is achieved compared to the bare Ta3N5 electrode. However, the photocorrosion of Co-Pi+Co(OH)/Ta3N5 electrode is still poor, in that only about 20% of the initial photocurrent remains after 2 h irradiation. The declining photocurrent trend is similar to that of IrO2 modified Ta3N5.²² In contrast, the NiFe-LDH/Ta3N5 electrode retains about 90% of the initial value even after 2 h of irradiation. The photocurrent increases, partially at the beginning stage, which is attributed to a "surface charging" process. This phenomenon indicates that surface-reaching holes are initially stored, which in turn increases a recombination flux of electrons at the surface.²⁶ XPS analysis after the stability test in Supporting Information Figure S10 shows a weak Ta 4p peak, and some cracks are also formed on the electrode surface during the PEC water splitting, evident in SEM as shown in Supporting Information Figure S4c. Thus, the slight deactivation might be associated with partial exposure of Ta3N5 to the electrolyte caused by these cracks. However, for the cobalt cocatalysts decorated NiFe-LDH/Ta3N5 electrode, the activity only mildly decreases in the initial 15 min but then exhibits a steady photocurrent of ~5 mA cm⁻² (about 80% of the initial activity) reliably for at least 2 h of irradiation. (Results for longer exposure times become less reliable and vary from sample to sample, which may reflect the finding that crack formation and pinholes in the cocatalyst layer may allow electrolyte penetration and thus a slow corrosion of the nitride phase.) Nevertheless, the results indicate that the NiFe-LDH layer efficiently prevents photocorrosion, restrains the recombination pathways, and improves the kinetic transport of photogenerated charge carriers away from the Ta3N5 surface. The observed photostability of Ta3N5 based systems at this high level of a photocurrent density (~5 mA cm⁻²) for several hours has not been achieved for any Ta3N5 nanorod arrays.

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of photogenerated carriers, and as a result enhances the photocurrent. Therefore, we attributed the improved PEC performance for NiFe-LDH/Ta$_2$O$_5$ mainly to the NiFe-LDH phase. In particular, the LDH/Ta$_2$O$_5$ junction facilitates charge transfer and improves the water oxidation. In the cyclic voltammogram experiments (Supporting Information Figure S11a-e), we observe that the NiFe-LDH without the Ta$_2$O$_5$ electrodes exhibits linear dependence with a positive slope from 0.2 to 0.5 V$_{RHE}$ which indicates a typical feature for an n-type semiconductor. EIS further reveals that the decrease of charge-transfer resistance is correlated to the increase of corresponding capacitance, which indicates that surface-reaching holes are immediately transferred away from the nitride.

## CONCLUSIONS

Using a through-mask anodization of Ta, regularly aligned Ta$_2$O$_5$ nanocolumns were grown. Upon nitridation in NH$_3$ atmosphere at 1000 °C, the structures were converted to Ta$_2$N$_x$ nanorod arrays that represent highly efficient anodes for PEC water splitting. By modification of the layers with NiFe-LDH, Co(OH)$_x$ and Co-Pi as cocatalysts, we obtained solar photocurrents of 6.3 mA cm$^{-2}$ at 1.23 V$_{RHE}$, which indicates a typical feature for an n-type semiconductor. More importantly, the electrode exhibits a remarkable stability against photocorrosion. A photocurrent of ~5 mA cm$^{-2}$ can be steadily maintained over 2 h irradiation. The combination of catalytic activity, stability, and decoration makes this new type of cocatalyst very promising to improve the photoelectrochemical performance of photoanodes in the field of energy conversion.

## ASSOCIATED CONTENT

### Supporting Information

Additional SEM images, XRD spectrum, XPS survey spectrum, PEC water splitting, CV diagrams, IPCE, and UV–vis diffuse reflectance spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interest.

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