Exploring the Origins of Improved Photocurrent by Acidic Treatment for Quaternary Tantalum-Based Oxynitride Photoanodes on the Example of CaTaO₂N

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Supporting Information

ABSTRACT: Quaternary tantalum-based oxynitrides ATa(O,N)₃, with electronic band gaps between 1.8 and 2.4 eV, are promising materials for photochemical water-splitting. The tailoring of their surface properties is a critical aspect to obtain efficient hole extraction. We report on the origin of improved photoelectrochemical (PEC) water oxidation by means of acidic treatment for this class of compounds on the example of cubic CaTaO₂N particles. We address the effect of acidic treatment by using complementary physical characterization techniques, such as X-ray photoelectron spectroscopy, electrochemical impedance spectroscopy, ¹H and ¹⁴N solid-state nuclear magnetic resonance (NMR) spectroscopy, electron microscopy, and electronic band structure calculations at the density functional theory level. In combination with PEC measurements, solid-state NMR indicates that the restructured surface displays a meaningfully higher concentration of terminating OH groups. Subsequent deposition of a nickel borate (NiBi) catalyst on the acid-treated surface yields a higher percentual upsurge of photocurrent in comparison to pristine CaTaO₂N. Our results highlight the application of solid-state NMR spectroscopy for understanding the semiconductor–catalyst interface in photochemical devices.

INTRODUCTION

An environment-friendly route for sustainable hydrogen production as a chemical fuel is photoelectrochemical (PEC) water splitting.¹⁻³ The oxygen evolution reaction (OER), as one of the two-half reactions during overall water splitting, is more demanding than the hydrogen evolution reaction because of inferior charge transport and slower kinetics of a four-electron reaction.⁴⁻⁵ Progress in PEC water oxidation on photoanodes, that is, semiconductor thin films coated with OER catalysts, has been mainly driven by oxide semiconductors.⁶ This is because of their chemical stability under operating conditions in neutral and alkaline electrolytes. For instance, the best-performing oxide photoanode is BiVO₄, with an electronic band gap of 2.4 eV being equivalent to a maximum theoretical photocurrent density of 7.4 mA cm⁻². Besides oxide materials with narrower band gaps, such as hematite,⁷,⁸ nitrogen-based compounds have emerged as semiconductor materials with higher theoretical photocurrent densities.

Semiconducting n-type metal carbodiimides and metal (oxy)nitrides are prospective photoanode candidates because of their usually narrower band gaps.⁹⁻¹⁰ For instance, the band gap of Ta₈N₉ is 2.1 eV and the experimentally achieved photocurrents of 12.5 mA cm⁻² are already very close to the theoretical limit of 12.9 mA cm⁻².¹¹ Nonetheless, the onset potential of 0.6 V versus the reversible hydrogen electrode (RHE) is still much higher than its flat-band potential of −0.2 V versus RHE. Quaternary oxynitrides AB(O,N)₃ (A = La, Ca,
Sr, Ba; B = Ta, Nb) crystallizing with a perovskite-related structure can exhibit variable band gaps ranging from 1.7 to 2.4 eV depending on their chemical composition.12−14 Recently, we reported the first successful synthesis of SrTaO2N nanowires that can be modified with functional coatings to achieve a hole-gradient extraction.13,15

Quaternary oxynitrides ATa(O,N)3 generally achieve a higher photocatalytic activity in comparison to their niobium counterparts ANb(O,N)3. This is because of the higher chemical stability of Ta5+, compared to Nb5+, which is more easily reduced to Nb4+. On the contrary, the high photocatalytic activity of the titanium-based oxynitride LaTiO2N (Eg = 2.1 eV) is attributed to the existence of Ti3+ at the surface region. Domen et al.16 demonstrated a twofold increase of chemical stability of Ta5+, compared to Nb5+, which is more easily reduced to Nb4+. The surface chemistry plays a decisive role for the photocatalytic activity of Ta3N5 because its surface consists of reduced tantalum ions forming a 2 nm thick TaN layer. This results in significant recombination of charge carriers at the surface. Acidic treatment can remove this surface layer and leads to an improvement in photocatalytic water splitting. Interestingly, the presence of oxygen in these etched samples is suggested by the XPS results, but the occurrence of hydroxyl species cannot be proven by infrared spectroscopy.18

We report on the origin of improved PEC behavior by means of acidic treatment for quaternary Ta-based oxynitrides on the example of CaTaO2N. The title compound can be classified as a semiconductor chemically lying between Ta3N5 and LaTiO2N. CaTaO2N crystallizes with a perovskite-related structure (space group Pnma) and has a band gap of 2.4 eV. The compound can be applied as a photocatalyst for either water splitting16−20 or CO2 reduction,21 as well as a nontoxic yellow pigment.22 We report on the first fabrication of a CaTaO2N photoanode and address the effect of acidic treatment by using complementary physical characterization techniques, such as X-ray photoelectron spectroscopy (XPS), electrochemical impedance spectroscopy (EIS), 1H and 11N solid-state nuclear magnetic resonance (NMR) spectroscopy, and electronic band structure calculations at the density functional theory (DFT) level.

**EXPERIMENTAL SECTION**

**Synthesis of CaTaO2N.** The oxide precursor Ca2Ta2O6 was synthesized by the solid state reaction of CaCO3 (99 wt %, Grüssing GmbH) and Ta2O5 (99.85 wt %, abcr GmbH). The mixture was heated at 1343 K for 24 h at a ramping rate of 10 K min−1 under ambient atmosphere and then cooled to room temperature at a rate of 10 K min−1.

For the conversion to CaTaO2N, 700 mg as-prepared white Ca2Ta2O6 powder was mixed with a flux of 300 mg NaCl (99.5 wt %, Grüssing GmbH) and 300 mg KCl (99.5 wt %, Grüssing GmbH). For ammonolysis, the mixed powder was placed into an alumina crucible in a tube furnace and was subsequently heated under a constant flow of NH3 (15 mL min−1) and H2 (5 mL min−1) at 1273 K for 15 h at a ramping rate of 10 K min−1. After cooling to room temperature, the product was washed thoroughly and filtered with distilled water to completely remove the flux agents. The yellow product was dried in an oven at 333 K for 8 h.

**Etching of CaTaO2N Powders.** 200 mg CaTaO2N was added into 4 mL freshly prepared aqua regia from HCl (~37%, Fisher Chemical) and HNO3 (65%, Fisher Chemical), and the suspension was stirred for 20 s. Afterward, the suspension was poured immediately into 1 L of distilled water, rinsed thoroughly during subsequent filtration and dried in an oven at 333 K for 8 h. The sample was denoted as CaTaO2N-A.

**Preparation and Etching of SrNbO2N Powder.** SrNbO2N was synthesized via the flux-assisted nitridation method. Briefly, 204.8 mg Nb2O5 (99.9 wt %, Sigma-Aldrich), 227.5 mg SrCO3 (99 wt %, Alfa Aesar), and 567.9 mg SrCl2·6H2O (flux; 99 wt %, Riedel-de Haen) were ground. The previous mixture was placed in an alumina crucible and heated under a constant flow of NH3 (15 mL min−1) and H2 (5 mL min−1) at 1173 K for 15 h at a heating rate of 10 K min−1. After cooling to room temperature, the product was washed thoroughly and filtered with distilled water to completely remove the flux agents, and dried at 333 K for 8 h. The acidic treatment was the same as for CaTaO2N powder. The powder X-ray diffraction (XRD) results are presented in Figure S1.

**Fabrication of CaTaO2N Photoanodes.** Thin film photoanodes were fabricated via the electrophoretic deposition (EPD) process followed by a necking treatment. In short, 24 mg as-prepared CaTaO2N or CaTaO2N-A were mixed with 6 mg of iodine in 30 mL of acetone, followed by 30 min sonication to obtain a uniform suspension. Two precleaned conductive fluorine-doped tin oxide (FTO) slides or one FTO slide and one titanium sheet were immersed in the above suspension with 1 cm distance, and a potential of 25 V was applied between them for 4 min. CaTaO2N particles were deposited on the electrode. After the electrodes were dried in air, 10 μL of 10 mM TaCl5 (99 wt %, abcr GmbH) methanol solution was dropped on the electrodes and dried. This procedure was repeated four times followed by annealing at 723 K for 1 h under a constant flow of NH3 (15 mL min−1) and H2 (5 mL min−1).

**Electrodeposition of the NiB Overlayer.** Electrodeposition of NiB onto CaTaO2N photoanodes was done in an electrolyte containing 1 mM Ni(NO3)2 and 0.1 M potassium borate (KB) buffer at pH 9.2 at a constant potential of 1.21 V versus 1 M Ag/AgCl for 15 s. The electrode was subsequently washed with deionized water. Scheme 1 shows the complete preparation procedure for the Ti/CaTaO2N-A/NiB photoanode.

**Powder XRD.** Powder XRD reflection patterns were recorded on a STOE STADI-P diffractometer (Cu Kα1, λ = 0.154056 nm).

**Scheme 1. Schematic Illustration of the Preparation of CaTaO2N Particle-Based Photoanodes**
were referenced to the C 1s core level (eV) at a constant pass energy of 100 eV. The binding energies O and 2 N, tested all possibilities, and identified the spectrum.14N shifts were referenced with respect to solid 536 scans with 1 s relaxation delay were collected for each spectrum. The relaxation delay of 5 s together with the signal transients with 5 s relaxation delay were accumulated for each spectrum. The14N NMR spectra were obtained through Casa XPS software.

**Scanning Electron Microscopy**. Scanning electron microscopy (SEM) images were acquired on a Leo Supra 35VP SMT (Zeiss). To investigate the chemical homogeneity and positions with 2 O and 2 N, and the 8 c positions with 6 O and 2 N, tested all possibilities, and identified symmetrically different structures with the help of pymatgen.29 Furthermore, the predicted structure of Wolff and Dronskowsk for CaTaO2N was also compared to our structural models.30 All the predicted structure of Wol and Dronskowski for different anion orders and assumed ordered compounds were built and structurally optimized: we used a 1 × 1 × 1 cell, filled the 4c positions with 2 O and 2 N, and the 8d positions with 6 O and 2 N, tested all possibilities, and identified symmetrically different structures with the help of pymatgen.29 Furthermore, the predicted structure of Wolff and Dronskowsk for CaTaO2N was also compared to our structural models.30 All structural optimizations for our 30 models and the calculations of the wavefunctions for the bonding analysis of all 31 structures were performed with periodic DFT in VASP31,32 with strict convergence criteria of ΔE < 10−7 (10−5) eV per cell for electronic (structural) optimizations, respectively. We used the projector augmented-wave method31,32 with a plane wave cutoff of 520 eV and the Perdew–Burke–Ernzerhof functional.33

The integrated crystal Hamilton overlap population (ICOHP) values and crystal Hamilton overlap populations (COHPs) were calculated with the help of Lobster 3.1.0.34–37 The following basis functions of the pbeVasp-Fit2015 basis set was used: 2s and 2p for O and N, 3s, 3p, and 4s for Ca, and 5p, 5d, and 6s for Ta.

**PEC Measurements**. PEC studies of the CaTaO2N particle-based photoanodes were measured in 0.1 M NaOH aqueous solution (pH 13) with a three-electrode system where a Pt wire and a 1 M Ag/AgCl electrode were used as a counter electrode and a reference electrode, respectively, under AM 1.5G simulated sunlight. The Nernst equation (ERHE = E1M

\[ \theta_{Ag/AgCl} + 0.059pH + E_{Ag/AgCl} \]

was used: 2s and 2p for O and N, 3s, 3p, and 4s for Ca, and 5p, 5d, and 6s for Ta.

**RESULTS AND DISCUSSION**

**Structural Characterization.** XRD patterns confirm the successful synthesis of the precursor Ca2Ta2O7 (Figure S2) and conversion to the perovskite-related structure of CaTaO2N as a single phase (Figure 1). No distinct differences in the diffraction angles and peak intensities were observed after the aqua regia treatment in the XRD patterns. This structural stability is similar to LaTiO2N if the acid-treatment is carried out only for a short period of time, that is, up to few minutes.16 The UV–vis absorption edge for CaTaO2N and CaTaO2N-A

![Figure 1. Experimental and simulated powder XRD patterns of CaTaO2N and CaTaO2N-A (ICSD 411139).](image-url)
is almost the same and around 500 nm (Figure S3); in agreement with the known value of CaTaO2N.21

SEM was employed to observe the morphology of the fabricated CaTaO2N photoanode. The electrode surface is covered by cubic particles in the nano- to micrometer range (Figure 2). The cubes also exhibit several pores, which is a known phenomenon occurring when transforming oxides into nitrides or oxynitrides.

Aqua regia has been reported to enhance the photocatalytic performance of LaTiO2N16 and Ta3N518 by removal of the inactive surface layers. However, for both reported cases the applied analytic techniques including XPS and FT-IR spectroscopy did not show any evidence for the presence of surface hydroxyl groups after acidic treatment. This lack of quantitative description of the etching effect for these two materials is because of the low sensitivity toward changes in the composition occurring at the surface. For the binary nitride, the enhancement in photochemical activity is believed to be a consequence of etching a TaN or amorphous TaO surface layer. In order to understand the origin of enhanced PEC performance for a quaternary oxynitride, we analyzed the photoanode by solid-state NMR.38

In Figure 3a the quantitative 1H MAS NMR spectra collected from as-synthesized and aqua-regia-treated CaTaO2N perovskite oxynitrides are shown. It should be noted that the spectra were acquired before the oxynitride was assembled into a thin film electrode. The untreated sample exhibits 1H signal patterns typical for inorganic surfaces with proton species in terminating hydroxyl moieties with a chemical shift around 1 ppm, as well as those from different adsorbed water layers (4−7 ppm). The 1H MAS NMR spectrum of the sample treated with aqua regia reveals a surface with a remarkably higher concentration of terminating OH groups, accompanied by increased and alternated signal intensities in the spectral region of 4−7 ppm. Our results corroborate the substantial surface modifications upon exposure to aqua regia, and therefore support the conclusion that these superficial adaptations are the key to improved PEC performance. In particular, the 1H MAS NMR spectra do not indicate the presence of hydrogen being incorporated into the structure from NH3 or H2 gas used as a reactive source during synthesis. Additionally, we have performed the same experiments on the quaternary niobium-based oxynitride SrNbO2N. Although the effect of increasing the concentration of surface −OH is smaller for SrNbO2N compared to CaTaO2N, it is still clearly visible (Figure S4). Similar to CaTaO2N, no changes could be observed in the complementary powder XRD patterns of SrNbO2N after the acid treatment (Figure S1).

The 14N MAS NMR spectra exhibit a single resonance at 270 ppm (Figure 3b), in agreement with previous reports.39,40 This signal conforms nearly perfectly to a single Lorentzian
function with full width at half maximum (fwhm) of 210 Hz, which indicates an absence of any significant structural/occupational disorder. The aqua regia treatment seems to have no effect on the $^{14}$N spectrum, aside from a minor increase in the baseline width of the peak. $^{14}$N is an integer-spin ($I = 1$) nucleus which would usually display substantial resonance broadening because of the interaction between the nuclear quadrupolar moment and the electric-field gradient from the nearby electron density. However, at 60 kHz MAS the absence of spinning sidebands indicates a particularly small interaction. This is confirmed by $^{14}$N NMR spectra acquired on static samples, which exhibit unusually narrow resonances with fwhm of $\sim 1450$ Hz. This indicates a quadrupolar interaction that is actually zero because of extraordinarily high symmetry of the nitrogen site in CaTaO$_2$N, in agreement with previous studies. On the contrary, to the previous reports on the Ta$_3$N$_5$ photocatalyst, we could not detect the presence of a binary TaN phase, containing partially reduced tantalum ions, in the $^{14}$N MAS spectra. This suggests the origin of the photocurrent enhancement after acidic etching (vide infra) to be different for quaternary tantalum-based oxynitrides. The presence of any paramagnetic Ta$^{5+}$ ions formed by reduction of Ta$^{5+}$ during treatment with aqua regia would in principle be detectable by both $^1$H and $^{14}$N NMR, with additional peaks being observed that are shifted from the main resonances by a paramagnetic shift. The absence of any such additional resonances indicates that there is no evidence for Ta$^{5+}$ reduction.

The surface composition of the CaTaO$_2$N-A/NiBi photoanode was investigated by XPS (Figure 3c,d). The Ta 4f spectrum shown in Figure 3c was deconvoluted into three doublets, which are summarized in Table 1, suggesting a multiphase composition, such as Ta$_3$N$_5$, Ta$_2$O$_5$, and TaON. The presence of Ta$^{5+}$ ions surrounded by nitride and oxide anions is in agreement with the coordination of tantalum ions in CaTaO$_2$N. No peaks stemming from reduced forms of Ta$^{5+}$ cations could be detected in the XP spectra.

In the case of the Ca XP spectra (Figure 3d), the Ca 2p$_{3/2}$ and Ca 2p$_{1/2}$ peaks centered at 346.5 and 349.8 eV suggest that the calcium atoms are rather atoms in oxygen–hydroxide systems than in salts (e.g., carbonate, chloride, sulphate, or nitrate). The $E_0$ values of the Ca 2p$_{3/2}$ peak in salts is usually in the range 347.1–348.6 eV.

Reaffirming XPS as a surface characterization technique, these results prove that the aqua regia treatment increases the atomic Ca/Ta ratio, we performed additional XPS experiments on the pure oxynitride powder, that is, without the Ni–B catalyst, before and after inserting the powder into aqua regia. Within the standard deviation of the experiment, the atomic ratio remained unchanged (Figure S6). It should be noted that the complementary Ta 4f spectrum shown in Figure 3c represents the composite photoanode CaTaO$_2$N-A/NiBi, where the electrocatalyst was electrochemically deposited by applying an anodic current. As such, the composite photoanode contains a relatively larger contribution of Ta$^{5+}$ stemming from Ta$_2$O$_5$ in comparison to the XP spectra of the bare oxynitride powder presented in Figure S6.

For the complementary TEM analysis of the assembled CaTaO$_2$N-A/NiBi photoanode, the high-angle annular dark field (HAADF) overview is shown in Figure 4a. The image reveals a large agglomerate that was mechanically removed from the electrode surface. This region was scanned and energy dispersive X-ray spectroscopy (EDX) data were collected at each probe position. The EDX spectra were analyzed for the presence of Ca, Ta, O, and N. Within the precision of the experiment, the agglomerate appears to be chemically homogenous. Integration over all of the EDX spectra is presented in Figure 4b. A clear peak from the TEM grid, Fe and Al from the stainless steel) are colored in gray.

Table 1. Binding Energies of Ta 4f$_{3/2}$ and Ta 4f$_{1/2}$ Peaks for the Identified Ta$_3$N$_5$, TaON, and Ta$_2$O$_5$ Species

<table>
<thead>
<tr>
<th>composition</th>
<th>Ta 4f$_{3/2}$ (eV)</th>
<th>Ta 4f$_{1/2}$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$_3$N$_5$</td>
<td>27.0</td>
<td>24.8</td>
</tr>
<tr>
<td>TaON</td>
<td>27.7</td>
<td>25.7</td>
</tr>
<tr>
<td>Ta$_2$O$_5$</td>
<td>29.1</td>
<td>27.0</td>
</tr>
</tbody>
</table>

Electronic Structure. The ordering of oxygen and nitrogen atoms in quaternary oxynitrides is considered to...
Ca bonds have antibonding states below the Fermi level. The Ca than in BaTaO$_2$N and the ICOHP values of the Ta strengths for a certain bond. This agrees well with the results. The ICOHP values can be interpreted as a measure of covalent interactions. Exemplarily, COHPs for the most stable structural model to the sum of all Ta–N ICOHP values. The stability of the structural model clearly correlates with the covalent bond strengths of the Ta–N bonds; (b) depiction of the COHPs for the Ta–N interactions. Kubo et al. have already detected the same findings based on charge densities. The tubes were assembled into a thin film photoanode by EPD on a titanium substrate. Photoanodes on this metallic substrate without necking treatment exhibited meaningfully lower photocurrents (Figure S7). The deposition of the tubes on titanium substrates yielded higher illumination-dependent current densities in comparison to thin films on conductive FTO-coated glass (Figure S8). This is because of the lower interfacial transfer resistance for photoelectrodes on metallic prepared substrates. Nickel borate (NiB$_x$) was electrochemically deposited as an OER catalyst. All prepared photoanodes develop an anodic current during linear square voltammetry (LSV) under solar illumination (Figure 6). Similar to many other quaternary oxynitrides, such as SrNbO$_2$N, the initial photocurrent occurs at around 0.2 V versus RHE. The initial cathodic current at low potentials has been observed previously for porous TaON on Ti substrates and has been described as the capacitive current. The necking treatment heightened the photocurrents in comparison to photoanodes without improvement of the interparticle electric conductivity (vide supra). The acidic treatment strongly enhances the current density of ca. 40 $\mu$A/cm$^2$ at 0.2 V versus RHE. Acid-treated oxynitride gave a higher percentual upsurge of oxidation activity, two separate electrodes were prepared: (i) before (CaTaO$_2$N) and (ii) after acidic treatment (CaTaO$_2$N-A). For both cases, postnecking treatment in the form of TaCl$_5$ impregnation followed by low-temperature ammonolysis was applied to enhance the interparticle electric conductivity. TheJournal of Physical Chemistry C

Figure 5. (a) Correlation of the energy relative to the most stable structural model to the sum of all Ta–N ICOHP values. The stability of the structural model clearly correlates with the covalent bond strengths of the Ta–N bonds; (b) depiction of the COHPs for the Ta–N interactions. The Ta–N bonds do not display any antibonding states below the Fermi level. In contrast, the Ta–O bonds have antibonding states below the Fermi level. The Ca–O and Ca–N interactions are nearly not covalent but mostly ionic in nature.

The ICOHP values can be interpreted as a measure of covalent strength for a certain bond. This agrees well with the results of Wolff and Dranskowski who found that Ta–N is responsible for the stability of the CaTaO$_2$N structures. Furthermore, we compared their structure predicted energetically to our structural models and found it to be only slightly more stable than the most stable structural model based in ref 28 (<1 kJ/mol energy difference per unit cell).

Our most stable structural models have Ta octahedra with 2 N and 4 O in cis configuration. In contrast to the Ta–N interactions, there is an anticorrelation between the stability of the structural model and the ICOHP values for the Ta–O interactions. Exemplarily, COHPs for the most stable structural model are depicted in Figure 5b. As expected, only the Ta–O and Ta–N bonds are of covalent character, the Ca–O and Ca–N bonds are practically not covalent but ionic. The Ta–O bonds comprise antibonding levels below the Fermi level where Ta–N are completely bonding. The presence of antibonding states for the Ta–O bonds and the ideal bonding situation for the Ta–N bonds is identical to the situation in BaTaO$_2$N. However, the Ta–N bonds in CaTaO$_2$N are even more covalent than in BaTaO$_2$N; they show an ICOHP value of $-5.7$ eV per bond in CaTaO$_2$N and an ICOHP value of $-4.6$ eV per bond in BaTaO$_2$N. In contrast, the ICOHP value of the Ta–O bond in CaTaO$_2$N is slightly less covalent than in BaTaO$_2$N ($-3.9$ vs $-4.2$ eV). With our COHP analysis, we can also confirm the Ta (5d)–N (2p) interactions to be dominating the Ta–N interactions.}

Figure 6. LSV of photoanodes CaTaO$_2$N, CaTaO$_2$N-A, and composite photoanodes, containing a NiB catalyst, CaTaO$_2$N/NiB, and CaTaO$_2$N-A/NiB. All photoanodes were subject to necking treatment with TaCl$_5$. Measurements were performed in 0.1 M NaOH electrolyte (pH 13) at a scan rate of 10 mV/s under sequentially interrupted AM 1.5G illumination (100 mW cm$^{-2}$).
layer to the catalyst because of the acidic modification of the oxynitride surface.

EIS and Mott–Schottky measurements were carried out on the prepared photoanodes. Figure 7 depicts typical EIS Nyquist plots of the photoanodes under visible light illumination. The interface layer resistance arising at the surface of the electrode can be estimated from the arc radius of Nyquist plots; a small arc radius indicates a high charge transfer efficiency. After the aqua regia treatment from Figure 7. This reduced charge transfer resistance and accelerated electron transfer induced an enhancement of anodic photocurrent (Figure 6).

After modification with the NiBi catalyst overlayer, both the pristine and acid-treated photoanodes exhibit a decline of the arc radius. The positive slopes of recorded Mott–Schottky plots depict that the n-type semiconducting behavior of CaTaO2N maintains after the acidic treatment (Figure 8). However, an obvious shift of the flat band potential ($V_{FB}$) value after the aqua regia treatment can be observed. The values were ~0.59 V versus RHE and ~0.62 V versus RHE for the CaTaO2N and CaTaO2N-A samples, respectively. Lee et al. reported a change of surface band bending of p-type GaN after aqua regia treatment. This behavior could also apply for the acid-treated CaTaO2N particles.

**CONCLUSIONS**

We have determined the origin of improved PEC activity by the acidic treatment for Ta-based quaternary oxynitrides on the example of CaTaO2N. The computed electronic structure of the latter resembles BaTaO2N because of antibonding states for the Ta=O bonds and the ideal bonding situation for the Ta=N bonds. CaTaO2N has been assembled for the first time into a photoanode and the origin of ameliorated photocurrent was investigated with solid-state NMR, XPS, PEC analysis, and EIS. The $^{14}$N NMR spectra indicate a high symmetry of the nitrogen signal before and after acidic treatment, while we could not detect signal stemming from other forms of (oxy)nitride phases. On the other side, $^1$H NMR spectra suggest that photocurrent enhancement upon acidic treatment arises from a more heterogeneous surface with a significantly higher concentration of terminating OH groups. This modification enhances the charge transfer at the semiconductor–catalyst interface for the CaTaO2N-A/NiBi photoanode and yields an upsurge in photocurrent. The nature of photocurrent improvement is distinct from previous reports on LaTiO2N because a reduction of the oxidation state for the cation of the AO4N2 octahedra would result in the formation of inactive surface layers, such as TaN. Our results highlight the application of solid-state NMR spectroscopy for the understanding of the bulk and surface chemistry in order to develop efficient heterojunction photoanodes.

**ASSOCIATED CONTENT**

* Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.9b09838.

Powder XRD patterns of SrNbO2N before and after acid treatment; powder XRD patterns of Ca3Ta3O9; Tauc plot for indirect allowed transition for CaTaO2N and CaTaO2N-A; solid-state NMR spectra at 60 kHz MAS of $^1$H for SrNbO2N; XPS Ta 4p and N 1s spectra of the Ti/CaTaO2N-A/NiBi photoanode; XPS Ta 4f and Ca 2p spectra of the CaTaO2N powder before and after acidic treatment; LSV of Ti/CaTaO2N-A photoanode without necking treatment; LSV of FTO/CaTaO2N photoanode with necking treatment; and chronoamperometry of Ti/CaTaO2N and Ti/CaTaO2N-A photoanode with necking treatment and NiBi (PDF) DFT calculations (ZIP)

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Notes
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