Structural Properties of NdTiO$_{2+x}$N$_{1-x}$ and Its Application as Photoanode

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ABSTRACT: Mixed-anion inorganic compounds offer diverse functionalities as a function of the different physicochemical characteristics of the secondary anion. The quaternary metal oxynitrides, which originate from substituting oxygen anions (O$^{2-}$) in a parent oxide by nitrogen (N$^{3-}$), are encouraging candidates for photoelectrochemical (PEC) water splitting because of their suitable and adjustable narrow band gap and relative negative conduction band (CB) edge. Given the known photochemical activity of LaTiO$_2$N, we investigated the paramagnetic counterpart NdTiO$_{2.5}$N$_{1.5}$ by DFT calculations. The electronic structure was explored both experimentally and theoretically at the density functional theory (DFT) level. A band gap ($E_g$) of 2.17 eV was determined by means of ultraviolet–visible (UV–vis) spectroscopy, and a relative negative flat band potential of −0.33 V vs reversible hydrogen electrode (RHE) was proposed via Mott–Schottky measurements. $^{14}$N solid state nuclear magnetic resonance (NMR) signals from NdTiO$_{2.5}$N$_{1.5}$ could not be detected, which indicates that NdTiO$_{2.5}$N$_{1.5}$ is a berthollide, in contrast to other structurally related metal oxynitrides. Although the bare particle-based photoanode did not exhibit a noticeable photocurrent, Nb$_2$O$_5$ and CoO overlayers were deposited to extract holes and activate NdTiO$_{2.5}$N$_{1.5}$. Multiple electrochemical methods were employed to understand the key features required for this metal oxynitride to fabricate photoanodes.

INTRODUCTION

The globally increasing energy demand, which has been mostly met by fossil fuels up to now, is an important challenge. Developing generation IV nuclear technology of high energy density is currently considered a promising strategy for matching that challenge. With respect to the utilization of solar energy to produce alternative fuels, photoelectrochemical (PEC) technology looks like a sustainable solution by splitting water into “green” energy carrier hydrogen under sunlight irradiation, irrespective of the additional challenge to store and ship hydrogen. To improve the efficiency of PEC cells, attempts have been extensively explored since the pioneering conception of water splitting over semiconducting TiO$_2$.2

Serving as the core components of a PEC cell, the semiconducting photoelectrodes responsible for capturing energy from sunlight drive the separation of holes and electrons for consecutive oxidation and reduction of water. The slow kinetics of the oxygen evolution reaction (OER) over n-type photoanodes has motivated scientists to explore materials to address these pivotal issues.3 The most investigated n-type oxide-based semiconductors have, however, a more positive conduction band (CB) edge than the reduction potential for H$^+$/H$_2$, resulting in a high overpotential for OER.4 Hence, the relatively positive CB position inherently requires more external bias to realize PEC water splitting.

Beyond metal oxides, mixed-anion inorganic compounds, such as oxyfluorides, oxynitrides, oxide–carbodiimides, oxy- sulfides, oxyhalides, and oxyhydrides, could offer diverse functionalities originating from the different properties of the secondary anion.5–8 Within the past two decades, transition-metal oxynitrides have emerged as promising photoactive materials because of their frequently higher theoretical solar-to-hydrogen efficiency. This is in particular promising for the quaternary metal oxynitrides because they can exhibit a smaller band gap than the ternary oxides and even than the binary nitride Ta$_3$N$_5$ ($E_g$ = 2.1 eV). The less electronegative element N and its more covalent interaction with the metal orbitals as compared to the O 2p orbitals induce an upward shift of the

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valence band (VB) in such compounds, resulting in higher light absorption capability towards the wide visible range. Domen et al. have demonstrated a niobium-based oxynitride BaNbO₃N photoanode with photodegradation up to 740 nm. It should be noted that different anion ordering will affect the band gap varying up to 0.6 eV, which was proven previously on the example of CaTaO2N. The proper band edge positions of quaternary oxynitrides generally straddle the redox potential of water, thereby making them promising visible-light-induced photoelectrodes for overall water splitting. Their negative CB edge positions give negative photocurrent onset potential, which makes metal oxynitrides generally interesting for photoelectrolysise.

The quaternary metal oxynitrides of general formula AB(O,N)₃ (A = alkaline-earth metal, lanthanide; B = Ta, Nb, Ti) exhibit different properties depending on their chemical composition. They are part of a large perovskite-like class of compounds whose synthesis, characterization, properties, and theory have been reviewed quite a while ago. The alkaline-earth-metal tantalum-based oxynitrides CaTaO2N, SrTaO2N, and BaTaO2N crystallize in different space-group symmetries, that is, orthorhombic, tetragonal, and cubic, as a result of the structural distortion factor caused by the cation symmetries, and theory have been reviewed quite a while ago. While their conduction band edge positions differ up to 0.82 eV, the bottom of the conduction band has been proposed to consist entirely of empty Ta 5d orbitals, not too surprising for pentavalent tantalum. In comparison to tantalum-based and niobium-based oxynitrides, the titanium-based quaternary oxynitrides, except LaTiO2N, have rarely been investigated for PEC applications. A study by Woodward et al. has shown that NdTiO2xNₓ−x and LaTiO2N crystallize in different space groups but exhibit similar photocatalytic activity for water splitting, which is better than for CeTiO3 and PrTiO3. Because the PEC performance is sensitive to the band alignment of the CB and VB edges with respect to the water redox potentials, we were interested to investigate the structural properties of NdTiO2xNₓ−x and explore its PEC water splitting activity.

**Experimental Section**

**Synthesis of NdTiO2xNₓ−x.** The Nd₃Ti₂O₇ oxide precursor was conventionally synthesized by the solid-state reaction (SSR) with KCl as a flux. In a typical synthesis, 1.5 mmol of Nd₂O₃ (99.999 wt %, Koch-Light Laboratories Ltd.), 3 mmol of TiO₂ (99.9 wt %, VWR Chemicals), and 1.5 mmol of KCl (99.5 wt %, abcr GmbH) were mixed and ground, followed by heating in air at 1423 K for 8 h. The product was cooled to room temperature and wash thoroughly with distilled water to remove residual flux. The dried Nd₃Ti₂O₇ precursor was placed into an alumina crucible and put in a tube furnace. The thermal ammonolysis was performed under a constant flow of NH₃ (15 mL min⁻¹) and H₂ (5 mL min⁻¹) at 1223 K for 15 h at a ramping rate of 10 K min⁻¹. This ammonolysis process was repeated three times with intermittent grindings. Fabrication of NdTiO2xNₓ−x Photoanodes. The NdTiO2xNₓ−x powder was assembled into a thin film on precleaned conductive fluorine-doped tin oxide (FTO) glass (2.2 mm thick, Sigma-Aldrich) via an electrophoretic deposition (EPD) process. Concisely, 20 mg of NdTiO₂Nₓ−x was dispersed in 30 mL of acetone containing 10 mg of iodine by 20 min sonication to obtain a uniform suspension. Two FTO slides were immersed into the suspension parallelly with an ~10 mm gap, and then a 35 V bias was applied between them for 1 min. The FTO/NdTiO₂Nₓ−x photoanodes were dried naturally in air. A NbCl₅ impregnation step, which was adapted from TaCl₅ and TiCl₄, was performed to improve the connection of particles. The FTO/NdTiO₂Nₓ−x photoelectrode was soaked in 0.1 M NbCl₅ (99.99 wt %, abcr GmbH) dissolved in ethanol for 10 s and dried on a hot plate at 423 K. After repeating this procedure for four rounds, the electrode was then annealed in air at 573 K for 1 h to obtain FTO/NdTiO₂Nₓ−x/NbO₂. The electrode was further decorated with a water oxidation cocatalyst, i.e., CoO₂. A 45 μL aliquot of 7 mM Co(NO₃)₂ dissolved in methanol was dropped on the FTO/NdTiO₂Nₓ−x/NbO₂ surface followed by annealing at 473 K for 1 h. The composite electrode was washed with distilled water.

**Characterization.** Powder X-ray diffraction (PXRD) patterns were recorded in the transmission mode on a STOE STADI-P diffractometer (Cu Kα radiation) equipped with a DECTRIS Mythen 1K detector. A UV–vis spectrophotometer (UV-2600, Shimadzu) was employed to characterize the optical properties with BaSO₄ as the reference. The IR spectra were acquired via a Nicolet Avatar 360 FT-IR spectrometer (Thermo Fisher Scientific, USA) with KBr as the reference. Scanning electron microscopy (SEM) images were collected via a Leo Supra 35VP SMT (Zeiss). High-angle annular dark-field (HAADF) images were collected on a JEOI-2100F in scanning transmission electron microscopy (STEM) mode.

**Solid-State NMR Spectroscopy.** The solid-state ¹H magic angle spinning (MAS) NMR spectrum was acquired at a magnetic field strength of 14.1 T (Larmor frequency 600.1 MHz) with a Bruker Avance III spectrometer equipped with a 3.0 mm MAS probehead and employing a MAS rate of 60.00 kHz. Acquisition involved a 90° high-power adiabatic pulses with a 5 MHz frequency sweep. All pulses operated at a nutation frequency of 210 kHz. A total of 256 signal transients with 5 s relaxation delay were accumulated. H shifts were referenced by using neat tetramethylsilane (TMS).

**Computational Methods.** First-principles DFT calculations were performed by using the Vienna ab initio simulation package (VASP). Projector-augmented-wave (PAW) potentials with the exchangecorrelation functional of Perdew–Burke–Ernzerhof (PBE) were adopted. Semicore states were included, yielding the valence shells of 5s²6s²p⁵s²p⁵d⁴, 3p³3p⁴4s⁴3d², 2p²p² and 2p⁴p² for Nd, Ti, N, and O, respectively. Note that the 4f electrons in Nd are treated as core electrons instead of valence electrons. The plane-wave energy cutoff was set to 600 eV. Meta-generalized gradient approximations (meta-GGA) with the new SCAN functional were used in structural relaxations with a Γ-centered Monkhorst–Pack k × k × k mesh. Full ion optimizations are obtained with a threshold of self-consistent energy difference less than 10⁻⁶ eV and all forces smaller than 10⁻³ eV Å⁻¹. In addition, the hybrid HSE06 functional was further used to obtain a more accurate band structure based on optimized structures that were obtained with the SCAN functional. In the density of states calculation, a denser 8 × 8 × 8 k-mesh was adopted.
Electrochemical Measurements. A conventional three-electrode setup was used to perform all the electrochemical measurements in 1 M NaOH electrolyte (pH = 13.6). The FTO slide deposited with NdTiO$_2$$\_$$^x$$N_1$$^-$ was used as a working electrode with an exposed geometrical surface area of ca. 0.79 cm$^2$. Platinum wire and a 1 M Ag/AgCl electrode were used as counter and reference electrodes, respectively. The recorded potential vs 1 M Ag/AgCl was converted subsequently vs RHE according to the Nernst equation $E_{\text{RHE}} = E_{\text{1 M Ag/AgCl}} + 0.059 \, \text{V} \times \text{pH} + E_{\text{Ag/AgCl}}$. The light source was 1 sun simulated solar irradiation (AM 1.5G, 100 mW cm$^{-2}$) generated by a solar light simulator (class-AAA 94023A, Newport) with an ozone-free 450 W xenon short-arc lamp. Mott–Schottky measurements were conducted by using the Gamry INTERFACE 1010T potentiostat/galvanostat/ZRA workstation at an ac amplitude of 5 mV and different frequencies under dark conditions. Electrochemical impedance spectroscopy (EIS) was measured at 1.0 V vs RHE in an ac potential frequency range of 20 kHz–0.2 Hz under an AM 1.5G illumination. The linear square voltammetry (LSV) curves were swept negatively at a scan rate of 10 mV s$^{-1}$, and chronoamperometry (CA) curves at a constant bias 1.23 V vs RHE were recorded with a potentiostat (PalmSens4, PalmSens BV). Open-circuit photovoltages (OCPV) were collected under chopped illumination.

RESULTS AND DISCUSSION

Structural Analysis. The topotactic transformation of oxides via nitridation has been frequently used toward the synthesis of metal oxynitrides, which can enhance the exploitation range of visible light.$^{35}$ The PXRD patterns of Nd$_2$Ti$_2$O$_7$ (Figure 1a) are characteristic of a material belonging to the family of compounds with a noncentrosymmetric structure having perovskite-type slabs (space group $P\bar{1}12_1$).$^{36}$ During ammonolysis at high temperature, the Nd$_2$Ti$_2$O$_7$ precursor was converted to an oxynitride through O$_2^-$/$N_3^-$ substitution (Figure 1b). The resulting compound from the ammonolysis was identified as NdTiO$_2$$^x$$N_1$$^-$ by means of PXRD, matching with the previous report ICSD 94764 (Figure 1a).$^{36}$ The product crystallizes in a distorted perovskite-related structure (space group $Pnma$).$^{34}$

After chemical conversion from Nd$_2$Ti$_2$O$_7$ to NdTiO$_2$$^x$$N_1$$^-$ through O$_2^-$/$N_3^-$ substitution, IR spectra have also been conducted to identify the bonding situation. As displayed in Figure 2a, the oxide precursor Nd$_2$Ti$_2$O$_7$ shows a typical spectral shape of lanthanide titanates Ln$_2$Ti$_2$O$_7$.$^{37,38}$ The resulting compound from the ammonolysis was identified as NdTiO$_2$$^x$$N_1$$^-$ by means of PXRD, matching with the previous report ICSD 94764 (Figure 1a).$^{36}$ The product crystallizes in a distorted perovskite-related structure (space group $Pnma$).$^{34}$

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Figure 2. (a) IR spectra of Nd$_2$Ti$_2$O$_7$ and NdTiO$_2$$^x$$N_1$$^-$, (b) $^1$H MAS NMR spectra of NdTiO$_2$$^x$$N_1$$^-$, The inset shows the zoomed $^1$H NMR signal from NdTiO$_2$$^x$$N_1$$^-$, (c) HAADF image of NdTiO$_2$$^x$$N_1$$^-$ particles.

Figure 1. (a) PXRD pattern of Nd$_2$Ti$_2$O$_7$ and NdTiO$_2$$^x$$N_1$$^-$ for reference, the corresponding simulated PXRD patterns are also shown, (b) Crystal structural evolution from Nd$_2$Ti$_2$O$_7$ to NdTiO$_2$$^x$$N_1$$^-$ through O$_2^-$/$N_3^-$ substitution. It should be mentioned that the composition of the ternary metal oxynitride has been previously reported to have an oxygen-rich composition NdTiO$_{2.1}$$^x$$N_{0.83}$, with a statistic O/N distribution (vide infra).$^{34}$

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ions. Most of the expected signal intensity is buried in the baseline as a broad, featureless bump. Only two narrow (albeit very weak) signals remain: at 7.3 and 1.4 ppm, which we assign to physisorbed water and hydroxyl groups, respectively. The general appearance of the spectrum is very similar to that collected from CeTiO$_2$N.39 Importantly, in contrast to CeTiO$_2$N, the $^{14}$N NMR signal from NdTiO$_2$+$^x$N$_{1−^x}$ could not be detected, which we attribute to the fact that NdTiO$_2$+$^x$N$_{1−^x}$ has a statistic O/N distribution over the anionic sites. This is in agreement with a previous report of Rosseinsky et al., who determined this deviation from the ordered structure NdTiO$_2$N to be the slightly oxygen-rich NdTiO$_2$.2N$_{0.8}$ with negligible O/N ordering.34 Because the O/N ratio may be modified under the anodic PEC operation, resulting from noncomplete surface passivation, we chose to denote to the title compound for the sake of clarity as NdTiO$_2$+$^x$N$_{1−^x}$. The successful incorporation of nitrogen has been proved by complementary experimental analysis (vide infra). Therefore, the unusually high local symmetry of nitrogen environments in these systems is not fully satisfied in NdTiO$_2$+$^x$N$_{1−^x}$.39 The HAADF image reveals the particle size of NdTiO$_2$+$^x$N$_{1−^x}$ to be $\sim$150 nm in diameter with regular shapes (Figure 2c).

Experimental Electronic Structure. UV−vis diffuse reflectance spectra depicted in Figure 3a were used to analyze the optical property of NdTiO$_2$+$^x$N$_{1−^x}$. A clear absorption edge at $\sim$610 nm was confirmed, which is characteristic for NdTiO$_2$+$^x$N$_{1−^x}$. The background absorption (tail) in the infrared region indicates the presence of Ti$^{3+}$ species originating from the partial reduction of Ti$^{4+}$.22,40 However, it is not possible to determine, based on the IR analysis, the quantitative Ti$^{3+}$/Ti$^{4+}$ ratio. The phenomenon is more common occurring for niobium- and titanium-based oxynitrides than for tantalum-based oxynitrides because of the higher chemical stability of Ta$^{5+}$ compared to that of Nb$^{5+}$ and Ti$^{4+}$.22,41−43 Another weak feature with respect to $^4$G$^5/2$ and $^4$F$^5/2$ f−f transitions on Nd$^{3+}$ was also observed. The $E_g$ was determined to be 2.17 eV by the Tauc plot derived (Figure 3b) from the UV−vis spectra, close to the previously reported value 2.1 eV for NdTiO$_2$+$^x$N$_{1−^x}$.22

It is generally known that the flat band potential ($V_f$) can be estimated via the Mott−Schottky equation:

$$\frac{1}{C^2} = \frac{2}{\varepsilon_0 \varepsilon F N_d} \left( V - V_f - \frac{k_B T}{\varepsilon} \right)$$

(1)

where C is the interfacial capacitance, $N_d$ the number of donors, V the applied voltage, $\varepsilon_0$ the electronic charge, $\varepsilon$ the dielectric constant of the semiconductor, $\varepsilon_0$ the permittivity of free space, $k_B$ Boltzmann’s constant, and T the absolute temperature. Therefore, the potential $V_f$ can be obtained by extrapolation of the linear portion to the x-axis intercept from the plot of (differential capacitance)$^{-2}$ against the electrode potential. The Mott−Schottky plots measured at 10, 100, and 1000 Hz are presented in Figure 3c. The sample developed positive slopes in plots as expected for n-type semiconductors. The capacitances were found to be frequency-dependent, revealing Fermi level pinning due to a midgap state.45 The $V_f$ was determined to be $\sim$0.33 V vs RHE from Figure 3c, which is very close to LaTiO$_2$N at $\sim$0.37 vs RHE.46 It is interesting to

Figure 3. UV−vis diffuse reflectance spectra of NdTiO$_2$+$^x$N$_{1−^x}$ (a) and the corresponding Tauc plot (b). (c) Mott−Schottky plots for the FTO/NdTiO$_2$+$^x$N$_{1−^x}$ electrode recorded at various frequencies in 1 M NaOH electrolyte (pH 13.6) under dark conditions. (d) Band structure diagram of NdTiO$_2$+$^x$N$_{1−^x}$ including Ti$^{3+}$ states.

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note that secondary linearity portions (blue dashed lines) in
the plots can be seen. In connection with the UV−vis
absorption discussion, the secondary linearity portions were
likely caused by shallow Ti3+ defects near the conduction
band.40,47−50 The sub-band originated from shallow Ti3+ states
and was estimated to be centered at
−0.03 V vs RHE, slightly
above the reduction potential of water. In combination with
the UV−vis analysis, the positions of both CB minimum and
VB maximum are therefore located approximately at
−0.33 V vs RHE and 1.84 V vs RHE, respectively. The band structure
diagram of NdTiO2N including Ti3+ states is depicted in
Figure 3d, together with the reduction and oxidation potentials
of water. The band positions of NdTiO2N,−x make it
theoretically suitable for overall water splitting on a single
absorber.

Calculated Electronic Structure. As the counterpart of
experimental analysis, we performed theoretical investigations
at the DFT level to elaborate more details of the electronic
structure for the title compound. Three crystal structures with
the same chemical compositions, but different N/O distributions,
were first created (Figure 4a), and the corresponding
lattice parameters and volumetric data are presented in Table
S1. Thermodynamically, the one that possesses the lowest
energy is much more likely to approach the experimental
structure (type 2, two nitrogen atoms in a cis-type
configuration) given thermodynamical control. The structure
configuration was therefore used for further electronic
structure calculation. The electronic band structure was
calculated along the high-symmetry path "Γ(0, 0, 0) −
X(1/2, 0, 0) − M(1/2, 1/2, 0) − Γ(0, 0, 0)". The results
produced by using the SCAN and HSE06 functionals are
depicted in Figure S1 and Figure 4b, respectively, in
combination with its density of states (DOS).51 Note that
because of the strong correlation for Nd 4f electrons, large self-
interaction error occurs when these 4f electrons are treated as
valence electrons. Indeed, it falsely describes the NdTiO2N as
metallic, while experiments confirm it to be semiconducting.52
Therefore, we used a pseudopotential that treats the 4f
electrons (orbitals) as core, accounting for their strong
contraction. A direct band gap of 1.36 eV at the Γ point was
obtained with SCAN, which is smaller than the experimental
value 2.17 eV. After having included the Hartree−Fock exact
exchange contribution (HSE06),53 it leads to a wider band gap
of 2.27 eV, in good agreement with the estimated experimental

Figure 4. (a) Three simulated structures for model NdTiO2N
composition, with different kinds of N/O distributions. The energies
are relative to type 2, the one that possesses the lowest energy. Type 2
is used for further electronic structure calculation. (b) Electronic band
structure and projected density of states using the HSE06 functional.
The Fermi level is set to zero. The electronic band gap is calculated to
be 2.27 eV. (c) Electronic band structure and projected density of
states with type 1 configuration.

Figure 5. SEM images of FTO/NdTiO2N−x photoanodes (a)
before and (b) after Nb2O5 and CoOx postmodification.
result. The additional calculation on the type 1 configuration, in which the N and O atoms have different local positions with type 2 structure, yielded a band gap value of 1.99 eV (Figure 4c), consistent with previous reports.\textsuperscript{19} From its projected density of states (DOS), one can also observe that the valence bands are predominantly of N 2p and O 2p character, while the conduction bands are of Ti 3d character.

**Characterization of Photoanodes.** Figure 5a shows the SEM image of NdTiO$_{2+x}$N$_{1-x}$ particles assembled as thin films on FTO. NdTiO$_{2+x}$N$_{1-x}$ particles were estimated to be around 200 nm in diameter with irregular shapes. After postnecking with Nb$_2$O$_5$ and CoO overlayers, the particles were maintained in the original shapes (Figure 5b).

The XPS technique was employed to analyze the surface composition of the as-prepared composite FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$/CoO electrode. The collected spectra of the active phases (Co 2p, Nb 3d, Ti 2p, N 1s, and Nd 4d) are presented in Figure 6 and Figure S2. Analyzing the structure of the electrode from outermost layers introduced by the subsequent covering FTO substrate, we find a cobalt phase with a chemical nature revealed by the XPS Co 2p spectrum (Figure 6a). The characteristic doublet of Co 2p$_{3/2}$ (780.2 eV) and Co 2p$_{1/2}$ (795.5 eV) with spin-orbit splitting of 15.3 eV and no clear satellite structure confirm the presence of OER cocatalyst CoO with the dominant role of low-spin Co\textsuperscript{3+}.\textsuperscript{43,61} In turn, in the XPS Nb 3d spectrum the positions of the spin–orbit 3d$_{5/2}$ (207.1 eV) and 3d$_{3/2}$ (209.9 eV) components as well as symmetric peak shapes indicate the formation of a Nb$_2$O$_5$ phase (Figure 6b) which can related to the photo-absorber particles.\textsuperscript{55} The core component of the studied semiconducting material is NdTiO$_{2+x}$N$_{1-x}$, and the elements were analyzed on the basis of the XPS Ti 2p, N 1s, and Nd 4d spectra (Figure 6c,d and Figure S2). The full width at half-maximum (FWHM) of the Ti 2p$_{3/2}$ and Ti 2p$_{1/2}$ peaks is high enough to suggest the presence of Ti in various chemical environments. This is understandable due to the incorporation of Ti$^{4+}$ into the NdTiO$_{2+x}$N$_{1-x}$ oxynitride structure. The Ti 2p$_{3/2}$ photoemission at 458.4 eV (with corresponding the Ti 2p$_{1/2}$ component at 463.9 eV) is attributed to Ti in Ti–O bonds, while that at 457.3 eV (Ti 2p$_{1/2}$ at 462.4 eV) is assigned to Ti in N–Ti–O bonds.\textsuperscript{56} These result suggest Ti$^{4+}$ cations locating in TiO$_6$–N$_6$ octahedra. Two peaks of N 1 spectra located at 395.8 and 400.1 eV were observed (Figure 6d); similar pair peaks have been reported for N-doped TiO$_2$ and (La, Sr)TiO$_2$N.\textsuperscript{57,58} The peak at binding energy of 395.8 eV indicates the incorporation of N into the metal oxynitride lattice. The peak at the higher binding energy of 400.1 eV can be attributed to either chemisorbed molecular N$_2$ on the surface or atomic β-N of TiN.\textsuperscript{57,58} The exact interpretation of the Nd 3d region is troublesome due to the overlapping O KLL peaks. Therefore, we decided to use the less frequently analyzed, but more easily interpreted, Nd 4d spectrum. The Nd 4d$_{5/2}$ photoemission observed at 121.9 eV clearly confirms neodymium presents in Nd$^{3+}$ state (Figure S2).\textsuperscript{59,60}

**Evaluation of Photoelectrochemical Properties.** Although NdTiO$_{2+x}$N$_{1-x}$ has the capability of absorbing a wide range of visible light, the photoelectrode fabricated by means of EPD offered negligible photoresponse upon chopped irradiation (Figure 7a). The low PEC performance of EPD-based photoelectrodes has been ascribed to the weak adhesion to the substrate and low interparticular electric conductivity.\textsuperscript{43,61} A postnecking treatment step was thus applied to the as-prepared particle-based NdTiO$_{2+x}$N$_{1-x}$ thin film by hydrolysis of the NbCl$_5$–ethanol solution, forming a thin Nb$_2$O$_5$ networking layer. As a consequence, the modified FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$ electrode yielded noticeable OER photocurrent compared to the as-deposited FTO/NdTiO$_{2+x}$N$_{1-x}$ photoelectrode. It should be mentioned that similar effects have been observed on Pb$_2$Ti$_4$O$_9$F$_2$, Pb$_2$Ti$_4$O$_9$F$_{1.2}$, and TaON particle-based thin film photoanode by modifying with Ta$_2$O$_5$ or TiO$_2$ driving from TaCl$_5$ or TiCl$_4$\textsuperscript{15,25,62}.

![Figure 6. XPS analysis on Co 2p (a), Nb 3d (b), Ti 2p (c), and N 1s (d) spectra of the FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$/CoO$_x$ electrode.](https://dx.doi.org/10.1021/acs.inorgchem.0c03041)
Because bare n-type semiconducting photoanodes tend to suffer from poor surface water oxidation kinetics, the photoexcited holes could thus accumulate at the surface and lead to photocorrosion. The photocurrent density of the FTO/NdTiO$_2$N$_{1-x}$ photoanode in conjunction with a known OER cocatalyst, i.e., CoO$_x$, was compared and presented in Figure 7a. The photocurrent was improved considerably because of enhanced reaction kinetics and efficient utilization of the photogenerated holes reaching the electrode surface for water oxidation, and a final photocurrent density of ca. 60 µA cm$^{-2}$ was developed at 1.23 V vs RHE. The photoresponse begins at very negative onset potential close to 0 V vs RHE (Figure 7a, enlarged range between 0 and 0.4 V vs RHE of Figure 7a), profiting from its negative flat band potential. The postamelioration effect of Nb$_2$O$_5$ and CoO$_x$ overlayers was also reflected in the CA curves measured at constant potential of 1.23 V vs RHE (Figure 7b). Both the LSV and CA curves exhibit obvious spikes caused by processes at the semiconductor surface upon switching illumination.

**Mechanism of Activation.** Besides the direct evidence provided by SEM in Figure S5, additional electrochemical analytic techniques were performed to reveal the reasons of the
strongly increased by means of Nb$_2$O$_5$ treatment. The augmented value of $N_d$ awakened the FTO/NdTiO$_{2+x}$N$_{1-x}$ from negligible photoresponse (Figure 7). A cocatalyst CoO$_x$ modification raised the $N_d$ slightly further, but the photocurrent was significantly advanced. These were ascribed to prolonged lifetime and boosted charge separation.

To probe the CoO$_x$ effect in more detail, complementary transient photocurrent (TPC) measurements were performed and are depicted in Figure 10a. After deposition of the CoO$_x$ cocatalyst, the greater initial anodic photocurrent spike, which originated from separation of photogenerated electron–hole pairs at the electrode/electrolyte interface, indicated that holes can be captured by the new active sites for water oxidation. The FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$/CoO$_x$ photoanode also had a remarkably longer photocurrent decay time than that of FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$, which can be attributed to the efficient separation and transfer of photogenerated charges. A cathodic current peak was observed upon turning off the light, and the current was restored to the initial dark level. The higher amount of cathodic charge was consistent with the longer photocurrent decay time. The quantitative decay times were calculated to be 0.34 and 1.27 s (Figure S4) for FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$ and FTO/NdTiO$_{2+x}$N$_{1-x}$/Nb$_2$O$_5$/CoO$_x$, respectively. The CoO$_x$ modification results in longer lifetime of the charge carrier.

Because surface states could lead to Fermi level pinning at the surface, ideal photoanodes with no Fermi level pinning would expect to produce an open circuit potential under dark conditions (OCP$_{dark}$) close to 1.23 V vs RHE. As marked with orange oval in Figure 10b, the OCP$_{dark}$ of bare FTO/NdTiO$_{2+x}$N$_{1-x}$ positively shifted from 1.12 to 1.18 V vs RHE due to altered surface trap states by necking with the Nb$_2$O$_5$ thin overlayer. Grafting the OER catalyst CoO$_x$ diminished the Fermi level pinning effect further; thus, the equilibrium potential OCP$_{dark}$ was pressed toward the water oxidation potential. For photoelectrodes, the difference between open circuit potential in dark and light, i.e., OCVP, is crucial. Incremental OCVP with sequentially Nb$_2$O$_5$ and CoO$_x$ overlayers was observed in Figure 10b (blue circle), which is equal to a higher driving force toward water oxidation and therewith enhanced photocurrent (Figure 7).

### CONCLUSIONS

In summary, the properties of one member of the titanium-based quaternary oxynitrates, i.e., NdTiO$_{2+x}$N$_{1-x}$, were investigated. The band gap of the mixed-anion compound NdTiO$_{2+x}$N$_{1-x}$ was determined to be 2.17 eV, only slightly different from the theoretical value calculated at the DFT level. Mott–Schottky measurements demonstrate that NdTiO$_{2+x}$N$_{1-x}$ possesses a relative negative CB edge located at around −0.33 vs RHE, more negative than the potential of water reduction. The VB edge was thus proposed to be 1.84 V vs RHE, indicating a band structure beyond the reduction and oxidation potentials of water. This makes the title compound theoretically able to perform overall water splitting on a single absorber. Furthermore, the solid-state $^{14}$N NMR signals of NdTiO$_{2+x}$N$_{1-x}$ could not be detected, confirming that NdTiO$_{2+x}$N$_{1-x}$ is not exactly stoichiometric in comparison to structurally related metal oxynitrates.

Examining the particle-based bare photoanode did not exhibit noticeable photocurrent. Exceptionally, a noteworthy augmented photocurrent was achieved after subjecting to postdeposition of Nb$_2$O$_5$ and CoO$_x$ overlay. SEM, EIS, and
Mott–Schottky analysis evidenced that the thin Nb_{2}O_{5} overlayer could enhance the connections between the NdTiO_{2−x}N_{x−x} particles and thus increased the charge carrier concentration, significantly facilitating charge transfer. OCPV and TPC measurements confirmed that the OER cocatalyst CoO_{x} overlayer can ameliorate the surface states and accelerate the utilization of surface photogenerated holes, therefore extracting deeper holes and prolonging their lifetime. Our results highlight the capability of NdTiO_{2−x}N_{x−x} as photocative material with a wide visible light absorption edge for PEC water splitting. Further efforts on synthesis of nanoscopic forms of the title compounds should improve the PEC efficiency by decoupling charge carrier transport from light absorption.

**ASSOCIATED CONTENT**

*Supporting Information*

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03041.

Lattice parameters and volumetric data for the studied NdTiO_{2−x}N_{x−x} systems; the electronic band structure and projected density of states; calculation of transient decay time (PDF).

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**Notes**

The authors declare no competing financial interest.

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