Ammonia is a key chemical feedstock for industry as well as future carbon-free fuel and transportable vector for renewable energy. Photoelectrochemical (PEC) ammonia synthesis from NO$_x$ reduction reaction (NO$_x$RR) provides not only a promising alternative to the energy-intensive Haber–Bosch process through direct solar-to-ammonia conversion, but a sustainable solution for balancing the global nitrogen cycle by restoring ammonia from wastewater. In this work, selective ammonia synthesis from PEC NO$_x$RR by a kesterite (Cu$_2$ZnSnS$_4$ [CZTS]) photocathode through loading defect-engineered TiO$_x$ cocatalyst on a CdS/CZTS photocathode (TiO$_x$/CdS/CZTS) is demonstrated. The uniquely designed photocathode enables selective ammonia production from NO$_x$RR, yielding up to 89.1% Faradaic efficiency (FE) (0.1 V vs reversible hydrogen electrode (RHE)) with a remarkable positive onset potential (0.38 V vs RHE). By tailoring the amount of surface defective Ti$^{3+}$ species, the adsorption of reactant NO$_3^-$ and $^2$NO$_2^-$ intermediate is significantly promoted while the full coverage of TiO$_x$ also suppresses NO$_2^-$ liberation as a by-product, contributing to high ammonia selectivity. Further attempts on PEC ammonia synthesis from simulated wastewater show good FE of 64.9%, unveiling the potential of using the kesterite-based photocathode for sustainably restoring ammonia from nitrate-rich wastewater.

1. Introduction

Ammonia (NH$_3$) is not only one of the most fundamental chemical feedstocks used for fertilizers and pharmaceuticals, but has been recently considered as an important energy carrier for the global hydrogen economy and carbon-free fuels.[1–3] Despite the potential increasing demand for ammonia, the current industrial ammonia synthesis still relies on the traditional energy-intensive Haber-Bosch reaction, which consumes 1–2% of the world’s energy supply and leads to ≈1% of global greenhouse gas emission.[4–6] In this regard, photoelectrochemical (PEC) ammonia synthesis is considered as one of the most promising strategies which enables the direct solar-to-chemical energy conversion.[7,8] However, compared to N$_2$ reduction reaction to ammonia, ammonia synthesis by NO$_x$ reduction reaction (NO$_x$RR) is more practical as NO$_x$ (i.e., NO$_3^-$, NO$_2^-$, and NO) is much more soluble in aqueous solution than N$_2$ whilst

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the cleavage energy of the N=O bond is much lower than that of the N≡N triple bond.\[^{9,10}\] In addition, NO\(_x\), one of the most widespread pollutants originated from anthropogenic activities,\[^{11,12}\] can accumulate and dissolve in water, resulting in the increasing NO\(_3^-\) concentration, which harms aquatic ecosystems and threatens the health of human beings.\[^{13,14}\] Previous attempts have been mainly focused on the reduction or denitrification of NO\(_3^-\) instead of selectively restoring ammonia.\[^{15–17}\] Therefore, PEC ammonia synthesis from NO\(_x\)RR is utilizing only renewable solar energy to produce useful chemicals or fuels via a sustainable route while the incorporation of PEC NO\(_3^-\)RR system into wastewater treatment process also enables circular economy and balances the nitrogen cycle (Figure 1). Despite the promise, it is challenging to realize selective ammonia synthesis from PEC NO\(_x\)RR due to the lack of robust photocathode materials with synergistically outstanding light absorption capability, efficient photogenerated charge transfer, and selective surface catalytic reaction.

In addition, although the process of NO\(_3^-\) reduction to NH\(_4^+\) possesses a favorable thermodynamic potential (0.88 V vs reversible hydrogen electrode [RHE]),\[^{18}\] the applied potential for electrochemical NO\(_3^-\) reduction to ammonia stays far below the hydrogen evolution reaction (HER) potential (0 V vs RHE).\[^{19–21}\] The resulted large overpotential can give rise to some competing reactions such as NO\(_3^-\)-to-N\(_2\) or HER with unwanted electron consumption, thereby retarding the NH\(_4^+\) Faradaic efficiency (FE) and yield.\[^{19,22,23}\] Generally, the reduction of NO\(_3^-\) to NH\(_4^+\) is associated with eight-electron transfer reaction processes with multiple reaction pathways.\[^{19–21}\] Previous studies on electrochemical NO\(_3^-\)RR have reported that the production of NH\(_4^+\) from NO\(_3^-\)RR is highly dependent on the adsorption of reactant such as NO\(_3^-\) and the intermediates (i.e., NO\(_2^-\) and NO\(_2\)).\[^{24,25}\] Moreover, it has been found that the interaction between reactant and catalysts can be modulated by tailoring the surface chemical states of the catalysts (i.e., surface defects) thereby altering the reaction pathway.\[^{19}\] For example, TiO\(_2\) nanotubes with oxygen vacancy have been demonstrated to improve the NO\(_3^-\) adsorption and suppress the by-product formation during the electrochemical ammonia synthesis.\[^{16}\] Similarly, defective CuO nanoparticles with controllable oxygen vacancy density has also been reported exhibiting improved NO\(_3^-\) adsorption ability.\[^{27}\] Nonetheless, the integration of defect engineered cocatalyst on robust photocathode for selective PEC ammonia synthesis directly from NO\(_x\)RR has not been studied before, due to the irreconcilable parasitic light blocking/absorption effect of commonly used cocatalyst induced poor light absorption and photogenerated charge transfer.

Recently, Cu\(_2\)ZnSnS\(_4\) (CZTS)-based photocathodes have attracted increasing research interest due to its excellent light harvesting capability, earth-abundance, and environmental-friendliness.\[^{28,29}\] After constructing p–n junction with CdS buffer layer and post-heat treatment, CdS/CZTS photocathode exhibits robust charge separation efficiency, which can enable an energetic photoinduced reaction driving force to power the PEC reactions.\[^{30,31}\] When using CZTS-based photocathode for PEC NO\(_3^-\)-to-ammonia reduction, it is critical to rationally incorporate active PEC cocatalyst with controllable surface defects and suppress accompanying competing reaction process to achieve high selectivity while attaining efficient

Figure 1. Schematic diagram of PEC NO\(_3^-\)RR from NO\(_x\) to NO\(_3^-\) effluent and finally converted to ammonia solution, which can be accordingly extracted or converted to fertilizers.
photogenerated charge transfer dynamics and energetic surface reaction kinetics. However, in-depth understanding of the synergy between photogenerated charge transfer behaviors and the surface reaction mechanism are still in its infancy.

Herein, we demonstrate highly selective PEC NH$_4^+$ synthesis from NO$_3^-$ by designing surface defects on TiO$_2$/CdS/CZTS for PEC ammonia synthesis from NO$_3$RR. The metal–organic-complex-derived TiO$_2$ was applied as an active overlay with good surface coverage via a spray-coating method. By tuning the spray-coating processing temperature, the ratio of defective Ti$^{3+}$ species is effectively tailored in the TiO$_2$ layer, which is proven by both experimental results and theoretical simulation to be beneficial for the adsorption of reactant NO$_3^-$ and *NO$_2$* intermediate. Meanwhile, reduced work function and prolonged photogenerated carrier lifetime are obtained, facilitating photogenerated charge transfer with efficient surface reaction kinetics. The optimal TiO$_2$/CdS/CZTS photocathode attains up to 89.1% FE toward ammonia with an appreciably positive onset potential (≈0.38 V vs RHE). To the best of our knowledge, our work is the first to report selective PEC ammonia synthesis from NO$_3$RR, through applying defect engineering strategy on the photocathodes.

2. Results and Discussion

Transition metals such as Fe, Cu, Ti, and Ni, and their oxides catalysts have shown their great potential for ammonia synthesis from NO$_3$RR due to their unique electronic structure for adsorption of electron-rich NO$_3^-$ as well as their advantages of low-cost and large-scale application potential. Among them, TiO$_2$ is considered as one of the most promising candidates serving as the cocatalyst due to its excellent electron transfer capability, high transparency, good stability, and feasible processing approaches. However, density functional theory (DFT) calculation on the NO$_3^-$ adsorption energy of pristine TiO$_2$ indicates a relatively low adsorption capability of NO$_3^-$

As illustrated in Figure S3, Supporting Information, the N–O bond from NO$_3^-$ tends to bond with the Ti$^{4+}$ from pristine TiO$_2$, with the adsorption binding energy calculated to be 1.6 eV (Figure S25, Supporting Information). Interestingly, the NO$_3^-$ adsorption energy can be significantly reduced by creating Ti$^{3+}$ (oxygen vacancy) on the surface. Thus, it is expected that Ti$^{3+}$ species from TiO$_x$ can effectively promote the adsorption of NO$_3^-$ reactant and thereby facilitate NO$_3$RR. Moreover, the overall PEC performance of TiO$_2$/CdS/CZTS photocathode is closely related to the uniformity, thickness, optical, and electrical properties, as well as footprint area of the cocatalyst TiO$_x$,[32] which could affect the light harvesting ability of underlying photoabsorber and the photogenerated carrier transfer. Therefore, to construct a highly efficient photocathode, TiO$_x$ cocatalyst with high transmittance for light penetration and controllable fabrication process is highly desired to meet the aforementioned requirement. In this regard, spray-coating of titanium diisopropoxide bis(acetylacetonate) (TIAA) is employed in this work since TIAA is widely used as TiO$_x$ precursor to fabricate anatase TiO$_2$ as electron transport materials for solar cells and sensors,[33] and spray-coating method can ensure the uniform deposition of TiO$_x$ layer with controllable thickness and surface coverage. The synthesis process of the TiO$_2$/CdS/CZTS photocathode is schematically illustrated in Figure 2a and detailed in the Experimental Section in Supporting Information. As shown in Figure S4, Supporting Information, the isopropyl ligands in TIAA can be easily hydrolyzed even at room temperature, while the decomposition of acetylacetone (AcAc) ligands responsible for the formation of Ti$^{3+}$ is a temperature-sensitive process. This allows the tunable concentration of Ti$^{3+}$ formation by controlling the processing temperature that alters the amount of remaining AcAc ligands.[34] The existence of Ti$^{3+}$ in the TiO$_2$ matrix indicates that the oxygen vacancies will be thereupon generated to maintain the electrostatic balance.[35] Specifically, CdS/CZTS films are placed on hot-plate of 200, 250, and 300 °C, respectively, during the spray-coating process (samples are denoted as TiO$_2$-200/CdS/CZTS, TiO$_2$-250/CdS/CZTS, and TiO$_2$-300/CdS/CZTS) to enable the hydrolysis-pyrolysis process of TIAA.

The morphology and the phase structure of the TiO$_2$/CdS/CZTS photocathode are first confirmed. As shown in Figure S5, Supporting Information, scanning electron microscopy (SEM) images reveal that the TIAA-derived TiO$_2$ materials obtained at different temperatures all exhibit as a compact and uniform layer on top of CdS/CZTS without obvious pinholes or cracks, which is critically important to suppress the possible competing reaction associated with underlying CdS/CZTS exposure. In addition, as observed from the cross-sectional scanning transmission electron microscopy images and energy-dispersive X-ray spectroscopy elemental mapping spectra shown in Figure 2b–i, the thickness of TiO$_2$ layer is ≈50 nm while the thickness of the entire TiO$_2$/CdS/CZTS photocathode is around 1 μm. Structural analysis from X-ray diffraction (XRD) indicates that all samples contain crystalline CZTS layer (PDF #26-0575) and CdS layer (PDF #21-0829) (Figure S6, Supporting Information). It is also noted that although no characteristic peaks of TiO$_2$ are evidenced from XRD due to the thin layer and low crystallinity of TiO$_x$, some ultrasmall crystalline TiO$_2$ nanoparticles have been observed from high resolution transmission electron microscopy in Figure S7, Supporting Information, which is assigned to the anatase TiO$_2$.

PEC NO$_3$RR performance of TiO$_2$/CdS/CZTS photocathodes via different spray-coating temperature is evaluated by a series of PEC characterizations in 0.1 m KNO$_3$ and 10 $\times$ 10$^{-3}$ m H$_2$SO$_4$ electrolyte. As evidenced in the linear sweep voltammetry (LSV) curves (Figure 3a), all the obtained TiO$_2$/CdS/CZTS photocathodes show obvious photocurrent density upon light illumination. In addition, positive onset potential is observed, reaching up to 0.38 V vs RHE for TiO$_2$-250/CdS/CZTS (photocathode current density of 20 μA cm$^{-2}$).[36] Moreover, the onset potential of CdS/CZTS is 0.24 V vs RHE (Figure S8, Supporting Information), which is more negative than that of TiO$_2$/CdS/CZTS photocathodes. This indicates that the coating of TiO$_2$ effectively lowers the NO$_3$RR overpotential. In addition, with the absence of NO$_3^-$ source, LSV curves of TiO$_2$/CdS/CZTS photocathodes in 0.1 m K$_2$SO$_4$ solution (Figure 3b) indicate an obviously lower current density, compared to the absence of NO$_3^-$ source, which further confirms the good activity of TiO$_2$/CdS/CZTS photocathodes for PEC NO$_3$RR. The chronoamperometry curves at 0 V vs RHE (Figure S9, Supporting Information) shows the same trend as LSV curves, with no obvious decay in the photocurrent density observed, indicating the good stability.
of the photocathodes throughout the 1 h test. More importantly, all photocathodes with sprayed TiO$_x$ show significantly better ammonia production performance than the CdS/CZTS photocathode counterpart. As observed from the NH$_4^+$ FE and corresponding yield rate of TiO$_x$-250/CdS/CZTS with various applied potentials in Figure 3c, it exhibits excellent PEC ammonia production performance among the tested potentials, with TiO$_x$-250/CdS/CZTS achieving 89.1% ammonia FE at 0.1 V vs RHE and the highest yield rate of 8.21 µmol h$^{-1}$ cm$^{-2}$ at −0.2 V vs RHE. The FE and corresponding yield rate of different temperature processed TiO$_x$/CdS/CZTS at −0.2V vs RHE is shown in Figure 3d, in which TiO$_x$-250/CdS/CZTS shows both higher NH$_4^+$ FE and yield rate compared to other two photocathodes. As evidenced from Figure S10, Supporting Information, NO$_2^-$ is determined as the by-product of the PEC NO$_x$RR of TiO$_x$-250/CdS/CZTS photocathode, while the NH$_4^+$ FE is more than 75% among all the tested potentials, indicating a good ammonia selectivity. Contrastingly, without the TiO$_x$ layer, CdS/CZTS photocathode shows poor ammonia selectivity, producing large amount of NO$_2^-$, which accounts for more than 70% FE with negligible amount of NH$_4^+$ (Figure S12, Supporting Information). This suggests that the uniform TiO$_x$ deposition ensuring full surface coverage of CdS/CZTS photocathode is required to suppress the associated competing reaction process, which is realized by our optimized spraying deposition as discussed before (Figure 2). In addition, as confirmed by the gas chromatography results, no toxic gas such as NO$_2$ is generated after the reaction. As is observed from Figure S13, Supporting Information, more than 80% of the current density is attained for TiO$_x$-250/CdS/CZTS at the end of 5 h reaction (−0.1 V vs RHE), indicating a good stability of the photocathode. This confirms that the TiO$_x$/CdS/CZTS photocathodes show excellent activity for NO$_3^-$ reduction with impressive ammonia selectivity. As far as we know, this is the first successful reported selective PEC ammonia synthesis from NO$_x$RR. In our system, CZTS is the photoabsorber absorbing solar light and producing photogenerated electron–hole pairs. The coating of a thin layer of n-type CdS forms the p–n heterojunction with p-type CZTS, contributing to the enhanced charge collection. TiO$_x$ layer on top of CdS/CZTS works as an effective cocatalyst for the reaction of NO$_x$RR to ammonia, which is demonstrated in Figure 3. This thin layer of TiO$_x$ can effectively accept photogenerated electrons from CZTS and promote the NO$_3^-$ reduction process.

As discussed above, the TiO$_x$-250/CdS/CZTS yields the best ammonia FE as well as the highest yield rate compared to other two samples. The effect of TIAA processing temperature on the PEC performance is likely to be related to the trade-off between charge transfer properties upon light illumination and surface catalytic activity of the obtained TiO$_x$ layer with distinct structural and chemical properties. A variety of characterization techniques have been applied to reveal the underlying...
mechanisms of the above hypothesis. At first, the band structure of TiO$_x$ synthesized at different spray-coating temperature is investigated since band structure and band alignment of the TiO$_x$/CdS/CZTS heterostructure play significant roles in tuning the charge carrier dynamics. While the band structure of CdS/CZTS has been comprehensively examined in our previous studies, further investigation is conducted to evaluate the band structure of TiO$_x$ synthesized at different temperature. As observed from the UV–vis spectra and the corresponding Tauc plots of bare TiO$_x$ samples synthesized with the same spray-coating conditions on glass substrates (Figure 4a and Figure S14, Supporting Information), the bandgap of TiO$_x$ increases with the spray-coating temperature. Specifically, TiO$_x$-200, TiO$_x$-250, and TiO$_x$-300 possess the bandgap of 2.93, 3.02, and 3.19 eV, respectively. Similar trend has been demonstrated in other works where TiO$_2$ layer was fabricated as the electron transporting layer in perovskite solar cells at low temperature.[37] Ultraviolet photoelectron spectroscopy (UPS) is used to determine the valence band position of TiO$_x$. From the UPS results in Figure 4b, work functions of the three samples are calculated by subtracting the cut-off binding energy with the photon energy (21.22 eV).[38,39] The onset energy regions shown in Figure S15, Supporting Information, present the distance between the valence band maximum and the Fermi level.[40] Valence band positions (vs vacuum) of TiO$_x$-200, TiO$_x$-250, and TiO$_x$-300 are estimated to be $-7.51$, $-7.44$, and $-7.28$ eV, respectively. Based on the UPS results and the calculated bandgap values, the band structure of TiO$_x$ is presented in Figure 4d. From the examined band alignment of CZTS, CdS, and TiO$_x$, it indicates that all samples possess suitable conduction band that can thermodynamically drive NO$_3^-$ reduction reaction. Interestingly, as illustrated in Figure 4c, the TiO$_x$-200 exhibits the highest work function of 4.78 eV, compared to that of TiO$_x$-250 (4.71 eV) and TiO$_x$-300 (4.70 eV). The differences in work function indicate a distinct electron transfer capability at the catalyst/electrolyte interface, in which a lower work function implies the presence of more energetic electrons on the surface of TiO$_x$ for NO$_x$RR.[38,41] The more energetic work function obtained from higher spray-coating temperature indicates the improved electron transfer within TiO$_x$-250 and TiO$_x$-300.

In addition to the band structure and band alignment, time-resolved photoluminescence (TRPL) spectroscopy is employed to probe the photogenerated carrier transfer and recombination behaviors of TiO$_x$/CdS/CZTS. As shown in Figure S16 and Table S1, Supporting Information, TiO$_x$-200/CdS/CZTS possesses the shortest carrier lifetime of 0.74 ns, indicating a relatively severe carrier recombination process, which might be caused by the excess structural defects (detailed discussions in subsequent section).[42,43] On the other hand, TiO$_x$-250/CdS/CZTS and TiO$_x$-300/CdS/CZTS exhibit more than twofold longer carrier lifetime compared to TiO$_x$-200/CdS/CZTS, which are 1.79 and 1.89 ns, respectively. The prolonged carrier lifetime reveals a more efficient charge transfer, consistent with the UPS results discussed above (Figure 4). Furthermore, electrochemical impedance spectroscopy (EIS) is used to evaluate the
interfacial charge transfer resistivity during the PEC reactions, in which the first arc (high frequency) represents the charge transfer within the photocathode and the second arc (low frequency) accounts for the resistance at the electrode–electrolyte interface.\textsuperscript{34,35} As shown in Figure S17, Supporting Information, their EIS indicates that all three samples show similar charge transfer resistance within the bulk with obvious different resistance corresponding to the surface reaction. TiO\textsubscript{x}-200/CdS/CZTS and TiO\textsubscript{x}-250/CdS/CZTS exhibit similar electrode–electrolyte interface resistance, which is smaller than that of TiO\textsubscript{x}-300/CdS/CZTS. This indicates that TiO\textsubscript{x}-250/CdS/CZTS and TiO\textsubscript{x}-300/CdS/CZTS have more efficient electron transfer at the photocathode/electrolyte interface to enable an energetic surface reaction kinetics. Based on the UPS, TRPL, and EIS results, it is believed that increasing spray-coating temperature results in the reduced work function of TiO\textsubscript{x}, which enhances the electron transfer and increases the carrier lifetime. Furthermore, it is known that apart from the photogenerated charge dynamics of the photocathodes, the surface reaction kinetics also plays an important role in achieving selective PEC ammonia production, which is closely related to the surface chemical states of the cocatalyst discussed as follows.

The surface chemistry of spray-coated TiO\textsubscript{x} with different temperatures is evaluated by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared (FTIR) spectroscopy (Figure 5a–d). The XPS Ti 2p spectra of all the samples (Figure 5a–c) consist of dominant peak located at 458.9 eV, corresponding to the presence of Ti\textsuperscript{IV} representing the Ti species in stoichiometric TiO\textsubscript{2}.\textsuperscript{46} Careful observation reveals that small characteristic peak at lower binding energy (457.6 eV) is evidenced, which can be assigned to the existence of Ti\textsuperscript{III} with oxygen vacancy (V\textsubscript{O}).\textsuperscript{47} The percentage of Ti\textsuperscript{III}/(Ti\textsuperscript{III}+Ti\textsuperscript{IV}) (Table S3, Supporting Information) decreases with the increasing spray-coating temperature, which is 8.33% for TiO\textsubscript{x}-200/CdS/CZTS, 7.31% for TiO\textsubscript{x}-250/CdS/CZTS, and 3.48% for TiO\textsubscript{x}-300/CdS/CZTS, respectively. This indicates that low-temperature spray-coating (200 °C) creates more unsaturated Ti\textsuperscript{III} species in TiO\textsubscript{x} when compared to the TiO\textsubscript{x} fabricated at 250 and 300 °C. In addition, O 1s spectra provided in Figure S18, Supporting Information, at the binding energy of 531.9 eV can be assigned to surface V\textsubscript{O}, which is another evidence for the formation of Ti\textsuperscript{III} species.\textsuperscript{48} Likewise, the V\textsubscript{O} amount also decreases with increasing spray-coating temperature, consistent with the trend observed in Ti 2p spectra (Figure 5).

In order to elucidate the formation mechanism of Ti\textsuperscript{III} from TIAA, FTIR analysis is further conducted to analyze the surface residual ligands of TiO\textsubscript{x} (Figure 5d). All samples demonstrated vibration peaks below 1000 cm\textsuperscript{-1}, which can be assigned to the Ti–O–Ti species in the TiO\textsubscript{x} matrix originated from the hydrolysis of TIAA.\textsuperscript{34} Moreover, the surface residual AcAc ligand that exhibits several stretching vibrations of C=O (1570 and 1526 cm\textsuperscript{-1}), C–H (1422, 1351, and 1283 cm\textsuperscript{-1}), and C–O (1025 cm\textsuperscript{-1})\textsuperscript{37} has also been detected from TiO\textsubscript{x}-200 and TiO\textsubscript{x}-250, which, however, becomes weaker in TiO\textsubscript{x}-300. Notable that the residual ligand evidenced from the FTIR is originated from the AcAc ligands, whereas the characteristic peaks of propyl ligand are not observed due to the easily hydrolyzed and pyrolyzed isopropyl ligand.\textsuperscript{49} The observed AcAc ligand residues reveal that the formation of Ti\textsuperscript{III} is mainly related to the sluggish and temperature-dependent hydrolysis process of TIAA. Therefore, it is proposed (as illustrated in Figure 5e) that during the hydrolysis and condensation of TIAA, TiO\textsubscript{x} matrix is formed while the existence of AcAc would enable the transformation of Ti\textsuperscript{IV} + HAcAc → Ti\textsuperscript{III} + ·AcAc and finally result in...
the presence of Ti\textsuperscript{3+} species and accompanying oxygen vacancy within the TiO\textsubscript{x} matrix.\textsuperscript{[50,51]} In addition, the localized π-bonding in the residual AcAc will overlap with the electron orbital of titanium to enable the change of the electronic structure of TiO\textsubscript{x}.\textsuperscript{[52,53]} implying the changes in the work function observed in Figure 4. As is evidenced by room-temperature EPR, the pristine TiO\textsubscript{2} exhibits no EPR signal (centering at \(g = 2.002\), Figure S19, Supporting Information) whilst a strong EPR signal is detected in TiO\textsubscript{x}-250, which can be ascribed to the formation of Ti\textsuperscript{3+} (oxygen vacancies).\textsuperscript{[54]} In addition, Raman spectra also indicates the formation of Ti\textsuperscript{3+} (oxygen vacancies, Figure S20, Supporting Information). \(E_{g}\) mode at 143 cm\(^{-1}\) of TiO\textsubscript{2} is shifted to higher frequencies in TiO\textsubscript{x}-250 compared to pristine TiO\textsubscript{2} (P25). According to previously reported works, this phenomenon can be assigned to the existence of oxygen vacancies in the lattice structure of TiO\textsubscript{x}.\textsuperscript{[55,56]} Based on the XPS, EPR, and Raman results, the formation of Ti\textsuperscript{3+} and oxygen vacancy is fully evidenced.

The presence of Ti\textsuperscript{3+} is a potential factor that leads to distinct ammonia selectivity among these three samples (see Figure 3). To further verify the effect of Ti\textsuperscript{3+} on the ammonia selectivity, control experiments using Aeroxide P25, a benchmark photocatalyst as TiO\textsubscript{2} cocatalyst, were performed.\textsuperscript{[57]} To obtain the surface oxygen vacancies and Ti\textsuperscript{3+} species of the P25/CdS/CZTS, post-treatment in H\textsubscript{2}/Ar (volume ratio of H\textsubscript{2}:Ar = 10:90) environment was conducted.\textsuperscript{[58]} As evidenced from its XPS spectra (Figure S21, Supporting Information), Ti\textsuperscript{3+} species were present in treated-P25 whilst only Ti\textsuperscript{4+} in the untreated P25/CdS/CZTS.\textsuperscript{[46]} The PEC ammonia synthesis performance of both treated and untreated P25/CdS/CZTS samples were evaluated based on the ammonia FE and yield rate. As shown in Figure S22, Supporting Information, the H\textsubscript{2}-treated P25/CdS/CZTS photocathode with Ti\textsuperscript{3+} surface demonstrated higher photocurrent density with similar onset potential obtained compared with the P25/CdS/CZTS reference (see the LSV curves of Figure S22a, Supporting Information), indicating a better catalytic activity originated from the defective surface with Ti\textsuperscript{3+}. For PEC ammonia production performance at 0 V vs RHE, untreated-P25/CdS/CZTS photocathode yields negligible amount of ammonia (Figure S22b, Supporting Information).

![Figure 5. a–c) Ti 2p spectra of TiO\textsubscript{x}/CdS/CZTS photocathode with different spray-coating temperatures. d) FTIR spectra of TIAA-derived TiO\textsubscript{x} with different spray-coating temperatures. e) Schematic diagram of hydrolysis process of TIAA to form TiO\textsubscript{x} with Ti\textsuperscript{4+}, Ti\textsuperscript{3+}, and oxygen vacancy (VO).](image-url)
Information), with only NO$_3^-$ detected as the by-product (up to 60% FE). This implies that the prompt desorption of NO$_3^-$ intermediate from the surface of P25 suppresses the further reduction of NO$_2^-$ into NH$_4^+$. On the contrary, the H$_2$-treated P25/Cds/CZTS produces ammonia at all the tested potentials (Figure S22c, Supporting Information) with up to 30% FE and 3.73 µmol h$^{-1}$ cm$^{-2}$ yield rate (at –0.3 V vs RHE). As expected, the amount of NO$_3^-$ generated from the treated P25/Cds/CZTS is significantly lower (only 15.6% NO$_3^-$ FE) than the untreated P25/Cds/CZTS photocathode. The results obtained from these control experiments signify that the enhanced ammonia selectivity is attributed to the presence of Ti$^{3+}$ species on the surface of the photocathode, which unveils the underlying mechanism for the enhanced ammonia selectivity of TiO$_2$-250/Cds/CZTS with more Ti$^{3+}$ when compared to TiO$_2$-300/Cds/CZTS.

It is also worth noting that although similar improved ammonia selectivity can be obtained via introducing Ti$^{3+}$ species in P25/Cds/CZTS, the PEC ammonia synthesis performance (i.e., photocurrent density, NH$_4^+$ FE, and yield rate) of H$_2$-treated P25/Cds/CZTS is still lower than those of TiO$_2$-250/Cds/CZTS, which is related to the poor surface coverage of P25 TiO$_2$ layer on the Cds/CZTS photocathode as shown in the SEM image (Figure S23, Supporting Information). The exposure of Cds results in higher NO$_2^-$ generation, which is similar to the Cds/CZTS photocathodes (Figure S12, Supporting Information). Furthermore, it is also known that the AcAc ligand in TIAA is electrophilic$^{31}$ which is beneficial for the adsorption of electron-rich NO$_3^-$ and NO$_2^-$ adsorption thereby facilitating ammonia production.

The studies confirm that the existence of Ti$^{3+}$, originated from either tunable hydrolysis of titanium precursor or reductive atmosphere treatment of crystallized TiO$_2$, can play a critical role in the selective ammonia production from NO$_2$/RR. In this regard, it is reasonable to deduce that the lower ratio of Ti$^{3+}$ in TiO$_2$-300/Cds/CZTS compared with that of TiO$_2$-250/Cds/CZTS, may reduce the NO$_2$/RR activity and corresponding ammonia selectivity, while the excessive residual AcAc in TiO$_2$-200/Cds/CZTS might induce highly defective TiO$_2$, which results in ineffective electron collection and serious charge recombination, and thereby poorer PEC performance.

In order to understand the effect of Ti$^{3+}$ species on the adsorption ability of NO$_2^-$ reactant and NO$_3^-$ intermediate, we carried out DFT calculations to investigate NO$_3^-$ and NO$_2$ adsorption energies on anatase TiO$_2$ (101) (pristine TiO$_2$) and TiO$_2$ (101) with Ti$^{3+}$ and oxygen vacancy (V$\_O$). As illustrated in Figure S3, Supporting Information, the O atoms from NO$_3^-$ adsorbed on pristine TiO$_2$ tends to bond with two adjacent Ti with the binding energy of 1.66 eV. When Ti$^{3+}$ serving as the adsorption sites, three types of NO$_3^-$ adsorbed on Ti$^{3+}$ sites have been investigated in order to better understand how Ti$^{3+}$ species interact with NO$_3^-$: First, in the case of a single Ti$^{3+}$ site (Figure S24a, Supporting Information), one of O atoms from NO$_3^-$ is adsorbed on Ti$^{3+}$, leaving the other two O atoms exposed as a “floating” manner, with a reduced binding energy (~0.75 eV) compared to pristine TiO$_2$ (1.66 eV). Second, when NO$_3^-$ is adsorbed on Ti$^{3+}$ and adjacent Ti$^{4+}$ pairs (Figure S24b, Supporting Information), the O atom of NO$_3^-$ occupies the V$_O$ site and bonds with Ti$^{3+}$ while the other one tends to be adsorbed on the neighboring Ti$^{3+}$. Moreover, the stronger N=O bond activation is evidenced at the Ti$^{3+}$ site with a larger N=O bond elongation from 1.21 to 1.37 Å. The further decreased binding energy (~1.64 eV) indicates an obvious enhancement of NO$_3^-$ adsorption ability with the presence of Ti$^{3+}$ and Ti$^{4+}$ pair. In addition, when NO$_3^-$ is adsorbed on adjacent Ti$^{3+}$ and Ti$^{4+}$ pair (Figure S24c, Supporting Information), one of O atoms of NO$_3^-$ occupies the V$_O$ site and the other O atom is adsorbed on the neighboring Ti$^{3+}$ site, leaving effective elongation of both N=O bonds and a further reduced binding energy (~2.07 eV). This suggests that Ti$^{3+}$ site can effectively activate the NO$_3^-$ in all three possibilities of NO$_3^-$ adsorption conditions, with bi-Ti$^{3+}$ sites as the optimal condition with lowest binding energy (Figure S25, Supporting Information). In addition, NO$_3^-$ adsorption energy on the pristine TiO$_2$ and bi-Ti$^{3+}$ sites is illustrated in Figure S26 and Table S4, Supporting Information. The adsorption energy of NO$_2$ adsorbed on pristine TiO$_2$ (Figure S26a, Supporting Information) is ~0.27 eV, much higher than that on bi-Ti$^{3+}$ species (~4.85 eV, see Figure S26b and Table S4, Supporting Information). One O atom from NO$_2$ tends to fill in V$_O$ site and bond with Ti$^{3+}$ while the other one tends to be bonded with another Ti$^{3+}$. This further indicates a strong adsorption ability of NO$_2^-$ intermediate with the formation of Ti$^{3+}$/V$_O$, which thereby suppress the liberation of NO$_2^-$ as by-product. Furthermore, the adsorption energy of NO$_2$ for Cds is calculated by DFT as shown in Figure S27 and Table S4, Supporting Information. The adsorption energy of Cds (110) is ~0.20 eV, which is even higher compared to pristine TiO$_2$ (Table S4, Supporting Information). This indicates the low NO$_2^-$ adsorption of Cds/CZTS for NO$_2$/RR, which thereby results in the high yield of NO$_2^-$ as the product. To verify the adsorption capability of NO$_2$, 0.1 m KNO$_3$ with 10 × 10$^{-3}$m H$_2$SO$_4$ is used as the electrolyte (pH = 4.9). As is seen from Figure S28, Supporting Information, very low photocurrent is observed for the Cds/CZTS, which is dramatically lower than using KNO$_3$ as the electrolyte (Figure S8, Supporting Information). In addition, the TiO$_2$-250/Cds/CZTS still exhibits considerable photocurrent in the NO$_2^-$ solution, suggesting superior NO$_2^-$ adsorption capability. Based on the above discussion and the proposed reaction pathway from NO$_3^-$ to ammonia in acidic condition shown in previous studies$^{[20,26]}$, we propose the reaction mechanism of PEC NO$_3^-$ to ammonia as illustrated in Figure 6. First, the TiO$_2$ derived from TIAA layer attains strong adsorption ability of NO$_3^-$ due to the creation of Ti$^{3+}$ as the electron donating site. Second, owing to the defective TiO$_2$ layer with suitable amount of Ti$^{3+}$ and V$_O$, the intermediate NO$_2^-$ is further adsorbed on the surface and reduced into NO. The H$^+$ presence in the acidic electrolyte can then facilitate the hydrogenation of NO to NOH and subsequent hydrogenation of NOH to NH$_2$OH, which is then converted to NH$_3$ as the target product. In the case of low Ti$^{3+}$ and V$_O$ concentration (such as P25/Cds/CZTS) and/or unfavorable work function (such as TiO$_2$-300/Cds/CZTS), NO$_2^-$ intermediate may be desorbed from the surface, leading to the formation of large amount of NO$_2^-$ as the by-product.

Therefore, by tuning the spray-coating temperature, favorable work function of TiO$_2$ and suitable band alignment of TiO$_2$/Cds/CZTS can be obtained with prolonged photogenerated carrier lifetime and improved electron injection efficiency. This enables an effective surface reaction kinetics with
lowered overpotential. More importantly, controllable hydrolysis of TIAA enables the formation of Ti$^{3+}$, acting as the active site for NO$_3^-$ and NO$_2^-$ adsorption during the reaction, while suppressing the NO$_2^-$ liberation and thus enhancing the NH$_4^+$ selectivity. Given that this is the first work that demonstrate a feasible PEC NO$_3^-$-to-ammonia reduction system, we have compared the performance of our photocathode to existing studies that conduct PEC ammonia production via N$_2$ (Table S5, Supporting Information). Notably, the PEC ammonia synthesis performance (in terms of NH$_4^+$ FE and operating potential) of our photocathode TiO$_x$/CdS/CZTS exhibits distinct superiority when compared to other reported studies on PEC ammonia production from N$_2$ reduction. Moreover, compared to these recent works on PEC NO$_x$RR, our result is among the best in terms of ammonia FE and better than those works considering the yield rate. Furthermore, the PEC ammonia synthesis from wastewater is attempted. The simulated wastewater containing 0.05 m NO$_3^-$, 0.05 m SO$_4^{2-}$, and 0.07 m Cl$^-$ (a typical composition from nitrate rich industrial wastewater or waste brine)$^{[59,60]}$ has been used to evaluate the feasibility of using TiO$_x$-250/CdS/CZTS photocathode for sustainably generating ammonia from wastewater. It is evidenced at −0.38V vs RHE, that 64.9% NH$_4^+$ FE with yield rate of 6.54 µmol h$^{-1}$ cm$^{-2}$ can be achieved (Figure S29, Supporting Information). This implies the as-obtained photocathodes show reasonably good selectivity for producing ammonia from simulated nitrate-rich wastewater, unveiling the potential of utilizing solar light to recover ammonia from wastewater. More interestingly, considerable performance of up to 38.3% NH$_4^+$ FE with a photocurrent density of −0.2 mA cm$^{-2}$ at −0.38 V vs RHE is achieved when using simulated wastewater containing only 3 × 10$^{-3}$ m NO$_3^-$ (Figure S30, Supporting Information).

3. Conclusion

We have demonstrated the feasibility of using a metal–organic complex-derived TiO$_x$ cocatalyst on CdS/CZTS photocathode for selective PEC ammonia synthesis from NO$_x$RR. It is found that the ratio of Ti$^{3+}$ species from TiO$_x$ overlayer can be effectively tailored by controlling the spray-coating temperature, which is confirmed to effectively promote the NO$_3^-$ and NO$_2^-$ adsorption as evidenced in experimental results and theoretical calculations. The trade-off between the photogenerated charge-transfer properties and the surface catalytic activity originated from the formation of Ti$^{3+}$/V$_0$ has been systematically investigated and discussed. With the suitable amount of Ti$^{3+}$ and efficient electron transfer performance evidenced by the reduced work function and prolonged carrier lifetime, TiO$_x$-250/CdS/CZTS photocathode attains up to 89.1% FE (0.1 V vs RHE) toward ammonia with a remarkably positive onset potential (=0.38 V vs RHE). In addition to the feasibility demonstration and mechanistic illustration, this work implements defect engineering strategy on kesterite photocathodes.

Figure 6. Proposed reaction pathway of NO$_3^-$ reduction to ammonia on TiO$_x$/CdS/CZTS photocathode.
via facile spray-coating method to ensure a full surface coverage of TiO$_2$ matrix on the CdS/CZTS photocathode, thereby effectively suppressing the competing reaction of NO$_2$ generation. This enables the obtained photocathodes to attain considerable activity for restoring ammonia from wastewater. It is believed that this work not only opens up a new pathway for PEC ammonia production but also provides important insight into defect engineering strategy for selective NO$_2$RR.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords
ammonia synthesis, defect engineering, kesterite photocathodes, NO$_2$ reduction, TiO$_2$.
[36] C. Li, T. Hisatomi, O. Watanabe, M. Nakabayashi, N. Shibata, K. Domen, J.-J. Delaunay, Energy Environ. Sci. 2015, 8, 1493.
[37] M. Lee, J. I. Park, H. Jeong, B. J. Kim, Y. Yun, H. J. Kim, H. Cho, S. Lee, Appl. Surf. Sci. 2020, 530, 147221.
[38] Y. Guo, T. Wang, Q. Yang, X. Li, Y. Liu, Y. Cao, H. Wang, H. Yu, F. Peng, L. Zhang, B. Zhang, K. Lu, Nano Energy 2018, 53, 97.
[39] Y. Lv, R. Yuan, B. Cai, B. Bahrami, A. H. Chowdhury, C. Yang, Y. Wu, Q. Qiao, S. Liu, W.-H. Zhang, Angew. Chem., Int. Ed. 2020, 59, 11969.
[40] Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong, C. Zhi, Energy Environ. Sci. 2021, 14, 3938.
[41] M. Yadav, A. Yadav, R. Fernandes, Y. Popat, M. Orlandi, A. Dashora, D. C. Kothari, A. Miotello, B. L. Ahuja, N. Patel, J. Environ. Manage. 2017, 203, 364.
[42] Z. Pei, S. Weng, P. Liu, Appl. Catal. B 2016, 180, 463.
[43] P. Yan, G. Liu, C. Ding, H. Han, J. Shi, Y. Gan, C. Li, ACS Appl. Mater. Interfaces 2015, 7, 3791.
[44] R. Zhang, M. Shao, S. Xu, F. Ning, L. Zhou, M. Wei, Nano Energy 2017, 33, 21.
[45] H. Zhang, Y. Zhao, S. Chen, B. Yu, J. Xu, H. Xu, L. Hao, Z. Liu, J. Mater. Chem. A 2013, 1, 6138.
[46] Y. Yang, P. Gao, X. Ren, L. Sha, P. Yang, J. Zhang, Y. Chen, L. Yang, Appl. Catal. B 2017, 218, 751.
[47] X. Liu, H. Xu, L. R. Grabstanowicz, S. Gao, Z. Lou, W. Wang, B. huang, Y. Dai, T. Xu, Catal. Today 2014, 225, 80.
[48] M. Mikula, Z. Beková, M. Hvojník, M. Hatala, M. Mikolášek, J. Mullerová, M. Jergel, P. Gemeiner, Appl. Surf. Sci. 2018, 461, 54.
[49] X. Chen, X. Peng, L. Jiang, X. Yuan, J. Fei, W. Zhang, Chem. Eng. J. 2022, 427, 130945.
[50] M. Lee, Z. Li, L. Zhu, X. Xie, X. Cui, Appl. Catal., B 2018, 224, 715.
[51] W. Macyk, K. Szaciłowski, G. Stochel, M. Buchalska, J. Kunczewicz, P. Labuz, Coord. Chem. Rev. 2010, 254, 687.
[52] Y. Guo, R. Zhang, S. Zhang, Y. Zhao, Q. Yang, Z. Huang, B. Dong, C. Zhi, Energy Environ. Sci. 2021, 14, 3938.
[53] M. Yadav, A. Yadav, R. Fernandes, Y. Popat, M. Orlandi, A. Dashora, D. C. Kothari, A. Miotello, B. L. Ahuja, N. Patel, J. Environ. Manage. 2017, 203, 364.
[54] Z. Pei, S. Weng, P. Liu, Appl. Catal. B 2016, 180, 463.
[55] P. Yan, G. Liu, C. Ding, H. Han, J. Shi, Y. Gan, C. Li, ACS Appl. Mater. Interfaces 2015, 7, 3791.
[56] R. Zhang, M. Shao, S. Xu, F. Ning, L. Zhou, M. Wei, Nano Energy 2017, 33, 21.
[57] H. Zhang, Y. Zhao, S. Chen, B. Yu, J. Xu, H. Xu, L. Hao, Z. Liu, J. Mater. Chem. A 2013, 1, 6138.
[58] Y. Yang, P. Gao, X. Ren, L. Sha, P. Yang, J. Zhang, Y. Chen, L. Yang, Appl. Catal. B 2017, 218, 751.