Photoelectrochemical Urea Synthesis from Nitrate and Carbon Dioxide on GaN Nanowires

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ABSTRACT: Semiconductor photoelectrodes can be used to synthesize urea from carbon dioxide and nitrate under solar light. We find that GaN nanowires (NWs) have inherent catalytic activity for nitrate conversion to nitrite, while Ag cocatalysts loaded onto GaN NWs further promote the performance of photoelectrochemical urea synthesis. Under optimized conditions, a high faradaic efficiency of 75.6 ± 2.6% was achieved at a potential of -0.3 vs reversible hydrogen electrode. Control experiments and theoretical calculations suggest that the high selectivity of urea originates from the facilitated C–N coupling between key intermediates of NO₂ and COO⁻ at an early stage of the reduction reaction. This work demonstrates the potential of GaN NWs with loaded Ag cocatalysts to achieve solar-powered urea synthesis with an efficiency higher than that of previously reported methods.

KEYWORDS: urea, nitrate reduction, carbon dioxide reduction, GaN, photoelectrode, metal cocatalyst

1. INTRODUCTION

Sustainable carbon and nitrogen recycling has emerged as a critical energy and environmental issue as we move toward a future with zero carbon emissions. Photoelectrochemical carbon dioxide (CO₂) reduction is a promising route for reducing CO₂ emission and producing value-added chemicals such as CO, HCOOH, CH₄, and multicarbon products.¹⁻⁴ The development of electrocatalysts for CO₂ reduction reactions has enabled the selective production of target chemicals in aqueous electrolytes. There are two main pathways for nitrogen recycling, including nitrogen (N₂)⁵⁻⁷ or nitrate (NO₃⁻) reduction reactions⁸⁻¹¹ to ammonia (NH₃), an essential raw material for modern chemistry. Both reactions offer a clean method for NH₃ synthesis compared to the conventional, energy-intensive, and carbon-emitting Haber–Bosch process.¹²,¹³ NO₃⁻ reduction is thermodynamically more feasible than N₂ reduction because the N≡O bond has much lower dissociation energy (204 kJ/mol) than the N≡N bond (941 kJ/mol), and NO₃⁻ is about 40,000 times more soluble in water than N₂.¹⁴ Therefore, high selectivity and productivity of NH₃ have been achieved by electrochemical NO₃⁻ reduction using various electrocatalysts.⁹,¹⁵,¹⁶

Urea [CO(NH₂)₂] is an essential fertilizer manufactured through a two-step process under high-temperature and high-pressure conditions. The Haber–Bosch process first yields NH₃, as depicted in the following chemical reaction: N₂ + 3H₂ → 2NH₃. Subsequently, NH₃ reacts with CO₂ to produce urea, following the chemical equation: 2NH₃ + CO₂ → CO(NH₂)₂ + H₂O.¹⁷⁻¹⁹ Recently, the electrochemical synthesis of urea has been demonstrated by simultaneous CO₂ reduction and N₂/NO/NO₃⁻/NO₂⁻ reduction at room temperature and under ambient pressure. For instance, PdCu–TiO₂,²⁰ Bi–BiVO₄ heterostructure,²¹ CuPc nanotubes,²² In(OH)₃ nanoparticles (NPs),²³ and polypyrrole-coated Pt electrode²⁴ produced urea from direct coupling of N₂ with CO₂. However, the faradaic efficiency (FE) has remained lower than 20% due to the difficulty of activating N₂. As alternatives to nitrogen sources, NO and NO₂⁻ have been electrochemically converted to urea with higher FE (11–43%) using Zn nanobelts,²⁵ Te–Pd nanocrystals,²⁶ ZnO nanosheets,²⁷ and Cu–TiO₂ catalysts.²⁸ More recently, oxygen-vacancy-enriched CeO₂,²⁹ In(OH)₃,³⁰ and In(OH)₃ catalysts as well as TiO₂–Nafion,³¹ Cu–Zn nanowires (NWs),³₂ Fe–Ni diatomic catalysts,³³ and Cu–N–C single-atom catalysts³⁴ have enabled the concurrent reduction of NO₃⁻ and CO₂ to urea in aqueous electrolyte. In particular, experiments with In(OH)₃ and In(OH)₃ have achieved high selectivity of urea generation (FE > 50%) at cathodic potentials of ~0.6 and ~0.5 V versus the reversible hydrogen electrode (V_RHE), respectively.³⁰,³¹ Theoretical

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calculations have suggested that the facilitated C–N coupling between \( \ast \text{NO}_2^- \) and \( \ast \text{CO}_2 \) intermediates on In(OH)\(_3\) at an early stage of the reaction can promote urea synthesis more effectively than the conventional C–N coupling between \( \ast \text{NH}_2 \) and \( \ast \text{CO}. \) Furthermore, rational design of the Cu–W bimetallic C–N coupling sites improved the performance of electrocatalysts, resulting in high FE\(_{\text{urea}}\) > 70%. However, the applied potential in electrochemical urea synthesis is still needed, and the product selectivity is still much lower than that of the individual CO\(_2\)-to-CO and NO\(_3^-\)-to-NH\(_3\) conversion reactions, which typically show faradaic efficiency above 80%.

This bottleneck in the electrochemical method can be mitigated by developing a photoelectrode. Semiconductor photoelectrodes generate a built-in potential under solar light, which can be used to shift the operating potential to a more positive value. This has been demonstrated in photoelectrodes for hydrogen evolution and CO\(_2\) reduction reactions. However, there has been no demonstration of any photo-electrode for urea synthesis to our knowledge. Therefore, there is an urgent need to screen semiconductor materials, understand their catalytic mechanisms, and optimize the physical and chemical structures for enhancing the performance of photoelectrochemical (PEC) urea synthesis. Semiconductor materials capable of efficiently and stably producing urea in aqueous electrolytes hold great promise as advanced photocatalysts for solar-driven urea production.

In this work, we found that GaN NWs grown on n’–p Si photoelectrodes exhibit catalytic activity for urea synthesis. An unprecedented high FE\(_{\text{urea}}\) of 74.5 ± 4.1% was achieved at −0.3 V\(_{\text{RHE}}\) by concurrent NO\(_3^-\) and CO\(_2\) reduction reactions. More noticeably, when Ag cocatalysts were loaded onto GaN NWs, the onset potential was positively shifted by ~0.1 V and the potential range for selective urea production (FE\(_{\text{urea}}\) > 45%) was significantly broadened. This resulted in a 4-fold increase in the urea production rate (4.4 ± 0.9 \( \mu \)mol/cm\(^2\)/h) at −0.6 V\(_{\text{RHE}}\). Control experiments and theoretical calculations
suggested that the GaN surface effectively produced NO\(_2\) intermediates, which then interacted with COO\(^{-}\) radicals and resulted in C–N coupling at the early stage of urea synthesis. This study shows that GaN can selectively produce urea by promoting C–N bonds from the NO\(_3\)\(^{-}\) and CO\(_2\).

2. RESULTS AND DISCUSSION

2.1. Ag Cocatalysts on GaN NWs/n\(^{+}\)–p Si Photoelectrodes. N-type GaN NWs were vertically grown along the c-axis of the wurtzite crystal on an n\(^{+}\)–p Si wafer by plasma-assisted molecular beam epitaxy under nitrogen-rich conditions (Figure 1a). Ag NP cocatalysts were then loaded onto the GaN NWs by photodeposition as described in the Experimental Section. When the photoelectrode is irradiated with light, the photoexcited electrons in the Si wafer move toward the GaN NWs and the Ag cocatalysts due to the built-in potential of the n\(^{+}\)–p Si junction and the applied cathodic bias. The photogenerated electrons can migrate to GaN and Ag surfaces without significant electrical resistance (Figure 1b) since there is negligible energy offset between the conduction bands of n\(^{+}\)-Si and n-GaN while the work function of Ag is below the conduction band edge of n-GaN.\(^{38,45}\) Subsequently, the electrons on the surfaces of GaN and Ag participate in the reduction steps that synthesize urea from the NO\(_3\)\(^{-}\) and CO\(_2\) under aqueous conditions.

We prepared three different Ag/GaN/Si photoelectrodes by changing the molar concentration of AgNO\(_3\) precursor solution used for photodeposition and denoted them as Ag\(_x\)/GaN/Si, where \(x\) is the molar concentration of AgNO\(_3\) in the unit of \(\mu\)M. As the amount of Ag precursor solution increased from 3 to 300 \(\mu\)M, the size of Ag cocatalysts became larger on GaN NWs (Figure 1c–e). In the case of Ag3 and Ag30, small NPs were formed on GaN NWs, whereas in Ag300, large microscale plate-shaped Ag particles were grown on the GaN surface. This indicates that the morphology and surface coverage of Ag cocatalysts, which are closely related to...
the photocurrent generation of the underlying GaN/Si photoelectrode and catalytic performance for urea synthesis, can be well-controlled. The microstructure of Ag30/GaN NWs was characterized using high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) after the Ag/GaN NW array was scraped from the Si wafer (Figures 1f and S1). Ag NPs ranging in size from 10 to 80 nm were observed on GaN NWs with a length of ∼400 nm and a diameter of ∼50 nm. The elemental distribution of N (red) from GaN NWs and Ag (cyan) from Ag NP was investigated by energy-dispersive X-ray spectroscopy (EDS) (Figure 1g). The N element was uniformly distributed over the GaN NWs, whereas Ag NPs were partially covered on the GaN surface. The area ratio of Ag NPs to GaN NWs was measured to be approximately 0.19, providing an estimate of the surface coverage of Ag NPs on GaN NWs (Figure S2a). In the high-resolution STEM images, Ag(111) planes with a d-spacing of 0.235 nm were predominantly observed (Figure S2b–d). The X-ray diffraction (XRD) patterns showed a prominent GaN (002) peak, indicating the presence of single-crystalline GaN NWs across all samples (Figure S3). Notably, the XRD pattern corresponding to Ag NPs was absent in Ag3/GaN/Si. However, a peak of Ag(111) emerged in Ag30/GaN/Si, corresponding to Ag NPs was absent in Ag3/GaN/Si.

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2.2. PEC Urea Synthesis from NO\textsubscript{3}\textsuperscript{−} and CO\textsubscript{2}. Linear sweep voltammetry (LSV) measurements were carried out to investigate PEC urea synthesis in CO\textsubscript{2}-saturated 0.5 M KNO\textsubscript{3} under AM 1.5 G 1 sun light illumination. The GaN/Si photoelectrode showed an onset potential (V\textsubscript{onset}) of −0.3 V\textsubscript{RHE}, where photocurrent density reaches −1 mA/cm\textsuperscript{2} (Figure 2a). The V\textsubscript{onset} was improved to −0.2 V\textsubscript{RHE} after loading Ag NPs on the GaN/Si photoelectrode, indicating that metallic Ag promotes cathodic reactions such as urea synthesis, NO\textsubscript{3}− reduction, CO\textsubscript{2} reduction, or H\textsubscript{2} evolution. However, when too many Ag microplates were loaded (Ag300/GaN/Si), the photocurrent density rapidly decreased because the opaque Ag cocatalyst blocked the incident light and limited the number of photocexcited charge carriers in the GaN/Si photoelectrode. Under dark conditions, no measurable photocurrent density was observed in any of the samples, highlighting the requirement of solar light for the PEC reaction. The photocurrent utilization and product selectivity were investigated by measuring the faradaic efficiency (Figure 2b) and production rate of urea (Figure 2c) at −0.3 and −0.6 V\textsubscript{RHE}. H\textsubscript{2} and CO gaseous products were measured by gas chromatograph, whereas urea, NH\textsubscript{3}, N\textsubscript{2}H\textsubscript{4}, and NO\textsubscript{3}− liquid products were spectro-colorimetrically measured (Figure S6). Interestingly, all photoelectrodes produced very high FE\textsubscript{urea} > 70% (Figure 2b) with a trace amount of NH\textsubscript{3}, H\textsubscript{2}, and CO products at −0.3 V\textsubscript{RHE} (Figure S7). However, when operating at −0.6 V\textsubscript{RHE} there was a notable decline in the faradaic efficiency and production rate of urea on the GaN/Si and Ag3/GaN/Si photoelectrodes likely due to the insufficient surface coverage of Ag NPs. In contrast, Ag300/GaN/Si retained high selectivity >50% at −0.6 V\textsubscript{RHE}. As a result, the Ag30/GaN/Si photoelectrode exhibited the highest production rate of urea at −0.6 V\textsubscript{RHE} among the tested samples due to the optimized balance between catalytic activity and photocurrent generation (Figure 2c). It is noticed that the production rate of urea may be seemingly low, although most photogenerated electrons participated in urea synthesis because of the very large number of electrons (16-electron) involved in the urea synthetic reaction compared to the NH\textsubscript{3} synthesis from NO\textsubscript{3}− reduction (8-electron), CO production from CO\textsubscript{2} reduction (2-electron), and H\textsubscript{2} evolution (2-electron).

The potential-dependent FE of the product was measured and compared on GaN/Si and Ag/GaN/Si photoelectrodes. The GaN/Si photoelectrode exhibited high FE\textsubscript{urea} > 70% at −0.3 and −0.4 V\textsubscript{RHE} (Figure 2d). To the best of our knowledge, such high urea selectivity has never been reported among any known semiconductor materials and photoelectrodes. At more negative potentials (<−0.5 V\textsubscript{RHE}), NO\textsubscript{3}− was produced as the major product. The missing total FE (<20%) may be attributed to the presence of undetected byproducts, such as nitrogen, acetamide, and formamide. Noticeably, Ag/GaN/Si showed a broader potential window (−0.1 to −0.6 V\textsubscript{RHE}) for high FE\textsubscript{urea} (Figure 2e). Ag/GaN/Si could achieve about a 4 times higher production rate of urea (4.4 ± 0.9 μmol/cm\textsuperscript{2}/h) than GaN/Si (1.0 ± 0.1 μmol/cm\textsuperscript{2}/h) at −0.6 V\textsubscript{RHE} (Figure 2f) because the higher photocurrent density flows at more negative potentials. Ag NPs supported on GaN NWs have the clear advantages of improving the efficiency and productivity of urea synthesis. Owing to the built-in potential generated by solar light and the excellent catalytic selectivity, the Ag/GaN/Si photoelectrode showed high FE\textsubscript{urea} = 75.6 ± 2.6% at a low potential of −0.3 V\textsubscript{RHE} compared to previously reported electrocatalysts measured in dark conditions (Figure 2g and Table S1). While the potential required to achieve a high FE\textsubscript{urea} of 75.6% is slightly more negative (−0.3 V\textsubscript{RHE}) for the Ag/GaN/Si photoelectrode compared to the recent CuWO\textsubscript{4} electrocatalyst (FE\textsubscript{urea} = 70.1% at −0.2 V\textsubscript{RHE}), this suggests that the integration of high-performing cocatalysts with GaN NWs/n"−p Si photoelectrodes has the potential to further shift the operating potential in a positive direction. Moreover, the stability of the Ag/GaN/Si photoelectrode was tested at −0.3 V\textsubscript{RHE} for 6 cycles (Figure 2b). Each cycle was performed for 1 h. The electrolyte was replaced with a fresh one after the reaction. The photoelectrode consistently produced urea with a high FE\textsubscript{urea} of 70.5 ± 5.0% and a production rate of 0.8 ± 0.1 μmol/cm\textsuperscript{2}/h, all while preserving its morphology (Figure S8) and chemical composition without any noticeable changes (Figure S9).

Control experiments were performed in three aqueous electrolytes of CO\textsubscript{2}-saturated 0.5 M KNO\textsubscript{3}, Ar-saturated 0.5 M KNO\textsubscript{3}, and CO\textsubscript{2}-saturated 0.5 M KHCO\textsubscript{3} to confirm that the C and N elements in urea originated from the CO\textsubscript{2} and NO\textsubscript{3}− sources, respectively. First, the GaN/Si photoelectrode (without Ag cocatalysts) showed more positive onset potential in the Ar-KNO\textsubscript{3} solution than the CO\textsubscript{2}-KNO\textsubscript{3} solution, and a low current density <1 mA/cm\textsuperscript{2} was measured in the CO\textsubscript{2}-KHCO\textsubscript{3} solution within the potential up to −0.6 V\textsubscript{RHE} (Figure 3a). This
means that GaN is more selective for NO$_3^-$ reduction reaction than CO$_2$ reduction and that CO$_2$ dissolved in the solution slows down the reaction kinetics likely due to lowering the local concentration of NO$_3^-$ near the photoelectrode. Potential-dependent FEs were also measured in Ar-KNO$_3$ (Figure 3b) and CO$_2$-KHCO$_3$ (Figure 3c). In the Ar-KNO$_3$ solution, NO$_3^-$ was the major product with FE$_{NO_3^-}$ > 70%, and minor products of H$_2$ and NH$_3$ were produced with FEs <20% (Figures 3b and S10a). In the CO$_2$-KHCO$_3$ solution, H$_2$ was the only product (Figures 3c and S10b). There was no CO evolution, despite the presence of the CO$_2$ reactant in the solution. These results reveal that GaN NWs can effectively reduce NO$_3^-$ to NO$_2^-$ but have no significant activity for the CO$_2$ reduction reaction. It should be noted that the GaN/Si photoelectrode, which cannot directly convert CO$_2$ selectively produced urea in the CO$_2$-KNO$_3$ electrolyte likely due to surface adsorbed intermediates such as *NO$_3$ that interact with CO$_2$ in the electrolyte and induce C–N coupling. This will be discussed in detail in the following section.

In stark contrast, Ag/GaN/Si showed improved LSV performance in the CO$_2$-KHCO$_3$ solution because the Ag catalyst is the well-known material for CO$_2$-to-CO conversion (Figure 3d).$^{47-49}$ Therefore, in the potential range of –0.1 to –0.6 V$_{RHE}$, where urea synthesis dominates in the CO$_2$-KNO$_3$ solution, there should be simultaneous reactions of NO$_3^-$ reduction and CO$_2$ reduction. The selectivity of NO$_3^-$ reduction was evaluated in the Ar-KNO$_3$ solution and it was found that most electrons were utilized for NO$_3^-$ production and some were consumed for NH$_3$ synthesis (Figures 3e and S11a). There was no urea production, indicating that carbon from the CO$_2$ molecule should be provided to form the C–N bond. In the CO$_2$-KHCO$_3$ solution, H$_2$ was the dominant product but CO was also produced with a FE$_{CO}$ of ~12% and a production rate of ~3.9 μmol/cm$^2$/h at ~0.6 V$_{RHE}$ (Figures 3f and S11b). The CO produced via CO$_2$ reduction reaction on the Ag/GaN/Si photoelectrode can react with N-containing intermediates (i.e., NO$_2^-$ and NH$_3$) produced via NO$_3^-$ reduction reaction, resulting in more efficient C–N coupling and urea synthesis as previously reported.$^{26,33}$ There was no urea production without the NO$_3^-$ reactant in the electrolyte, confirming that urea is produced from both CO$_2$ and NO$_3^-$ reactants. Furthermore, the isotope labeling test supported that NH$_3$ one of the products generated from NO$_3^-$ reduction, indeed originated from NO$_3^-$ in the electrolyte (Figure S12).

Inspired by Ag cocatalysts that can improve urea selectivity and productivity by enhancing CO generation, Au cocatalysts, known as efficient CO evolution catalysts,$^{50,51}$ were loaded onto GaN/Si photoelectrodes and tested as proof-of-concept experiments for PEC urea synthesis (Figure S13). The size of the Au NPs became larger as the precursor solution concentration increased from 6 to 600 μM. Similarly, the intensities of Ga 2p$_{3/2}$ and N 1s XPS spectra gradually decreased and those of Au 4f XPS spectra increased with Au loading (Figure S14). Among the three photoelectrodes, Au60/GaN/Si showed the best LSV performance in CO$_2$-saturated 0.5 M KNO$_3$ due to the optimal surface coverage of Au NPs (Figure S15a). Au60/GaN/Si showed a high FE$_{\text{urea}}$ = 76% at ~0.2 V$_{RHE}$ and a high production rate of urea = 2.1 μmol/cm$^2$/h at ~0.6 V$_{RHE}$ which outperformed the GaN/Si photoelectrode and was slightly inferior to the Ag/GaN/Si photoelectrode (Figure S15b). However, as the applied potential was increased to ~0.4 V$_{RHE}$ the Au/GaN/Si photoelectrode experienced a significant decrease in FE$_{\text{urea}}$ to <1% and an increase in faradaic efficiency for NH$_3$ to 55% (Figure S16a,b). This suggests that Au NPs inherently have higher activity in converting NO$_3^-$ to NH$_3$ compared to Ag.

Figure 3. LSV curves of (a) GaN/Si and (d) Ag/GaN/Si measured in CO$_2$-saturated 0.5 KNO$_3$, Ar-saturated 0.5 M KNO$_3$ (Ar-KNO$_3$), and CO$_2$-saturated 0.5 M KHCO$_3$ (CO$_2$-KHCO$_3$). Faradaic efficiency of H$_2$, CO, NH$_3$, NO$_2^-$, and urea for GaN/Si in (b) Ar-KNO$_3$ and (c) CO$_2$-KHCO$_3$. Faradaic efficiency for Ag/GaN/Si in (e) Ar-KNO$_3$ and (f) CO$_2$-KHCO$_3$. Urea was not produced in either Ar-KNO$_3$ or CO$_2$-KHCO$_3$. 

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NPs, thereby resulting in a large deviation in urea production. The stability of Au NPs was confirmed by negligible degradation of FE$_{\text{urea}}$ or the production rate during the 8 cycles of reaction (Figure S16c). Furthermore, Ag and Au

Figure 4. (a) Free energy profile of urea production on GaN without reduction of CO$_2$ to CO, including the crucial first step involving C–N bond formation, and subsequent reduction on the carbon site with further C–N bond formation and reduction. (b) DFT-optimized structures and reaction equations for each step.

Figure 5. (a) Free energy profile of urea production on GaN with Ag particles. Ag particles reduce CO$_2$ to CO, so the C–N bond formation is facilitated by the reaction of CO with either *NO$_2$ (blue) or *NO$_2^-$ (red) intermediates. This is followed by further reduction and the second C–N bond formation. (b) Corresponding DFT-optimized structures and reaction equations for each step.
catalysts were directly coated on the n-p Si photoelectrodes by photodeposition (Figure S17), and the PEC measurements were carried out in CO₂-saturated 0.5 M KNO₃ (Figure S18). Even with Ag and Au catalysts, the Si photoelectrodes exhibited very low photocurrent densities (<0.7 mA/cm² (Figure S18a) and low selectivity of urea (FE<sub>urea</sub> < 10% at ~0.4 V<sub>RHE</sub>) (Figure S18b), meaning that GaN NWs play a key role in reducing NO<sub>3</sub>⁻ and stabilizing reaction intermediates for C-N coupling and consequent urea production.

2.3. Density Functional Theory Study on the Catalytic Mechanism. We have applied density functional theory (DFT) to investigate the catalytic mechanism of urea production from CO₂ and NO<sub>3</sub>⁻, with an emphasis on the key step associated with C-N bond formation and competing pathways on GaN (Figure S19). Formation of urea by the reduction of CO₂ and NO<sub>3</sub>⁻ involves a 16-electron reaction with multiple steps along a complex reaction pathway (Figure 4). The crucial step is formation of the C-N bond, followed by subsequent reduction on the carbon site with further C-N bond formation and reduction. The relative energies of the reaction steps shown in Figure 4a correspond to the minimum energy structures shown in Figure 4b and are summarized in Table S2. The initial step of the mechanism involves adsorption of NO<sub>3</sub>⁻ in a bidentate mode with two oxygens bound to adjacent gallium sites. NO<sub>3</sub>⁻ is formed on the surface upon the further reduction and release of a water molecule. At this stage, the NO<sub>3</sub>⁻ can either be reduced to NO<sub>2</sub>⁻ or react with the adsorbed COO⁻ radical on the GaN surface (Figure 4b). Since both reactions are exergonic, the crucial C-N bond formation step proceeds in competition with formation of NO<sub>2</sub>⁻ which can desorb from the surface or remain on the surface to be subsequently reduced to NH<sub>3</sub>. After formation of the C-N bond, further reduction of the O₂N–CO₂⁻ species is thermodynamically downhill (see also Figure S20). The second C-N bond formation involves the OC-NH intermediate and coadsorbed NH₃. The resulting intermediate forms urea upon reduction. Therefore, after the first C-N coupling has taken place, formation of urea is energetically very favorable. We note that further reduction of NO<sub>2</sub>⁻ to NO (and subsequent reduction to NH₃) is energetically uphill, making NO<sub>2</sub>⁻ an important side product (Figure S21). Our calculations clearly show the negative potential that is needed to reduce CO₂ to CO on the GaN surface, in agreement with experimental results, while temporary production of the COO⁻ radical on the surface is thermodynamically favorable (Figure S22). Overall, our calculations suggest that the crucial step in urea production is the initial C-N bond formation that competes with NO<sub>2</sub>⁻ formation since both reactions are exergonic (Figure S23). Remarkably, CO formation is disfavored, so the C-N coupling takes place between the coadsorbed NO<sub>2</sub> and COO⁻ through a radical coupling mechanism. Thus, stabilization of the COO⁻ radical on the GaN surface allows for C-N bond formation without forming CO as in electrochemical processes.

When a cocatalyst that can electrochemically reduce CO₂ to CO, such as Ag<sub>47</sub>–49 is present, the initial C-N bond formation is significantly facilitated, as shown in Figure S5. While the reduction to NO<sub>2</sub> and the formation of the second C-N bond remain the same, the initial coupling between carbon and nitrogen proceeds differently when CO is available. Since CO has weak adsorption on silver (Table S3, in agreement with references),<sup>25</sup> CO can approach the GaN surface and react with the adsorbed NO<sub>2</sub> intermediate to form the O,N–CO intermediate. In contrast to the coupling with COO⁻, this facilitates urea production by making exergonic all subsequent catalytic steps after the NO<sub>2</sub>. Additionally, C-N bond formation by reaction with the adsorbed NO<sub>2</sub>⁻ intermediate is found to be thermodynamically accessible, although it did not react with CO₂. Therefore, the nitrite formation that leads to the main side product on GaN can still react by coupling to CO and form urea.

While C-N bond formation on GaN between adsorbed NO<sub>2</sub> and CO is favorable, it is unlikely on the Ag NPs, as shown in Figure S24. This is shown by the formation free energy of the O₃N–CO intermediate from coadsorbed NO<sub>2</sub> and CO on a Ag(111) surface, which is the most common facet of the Ag NPs. Therefore, the Ag cocatalyst facilitates urea production by forming CO, as species that can diffuse toward the GaN and react with either NO<sub>2</sub> or NO<sub>2</sub>⁻ intermediates adsorbed on the surface to form the C-N bond.

3. CONCLUSIONS

In summary, we have demonstrated an efficient GaN/Si photoelectrode for PEC urea synthesis from simultaneous NO<sub>3</sub>⁻ and CO₂ reduction reactions under solar light. The built-in potential in n-p Si and the inherent catalytic activity of GaN NWs led to the selective synthesis of urea at a low overpotential. Moreover, Ag and Au cocatalysts loaded onto GaN NWs improved the performance of PEC urea synthesis, resulting in a high FE<sub>urea</sub> of 75.6 ± 2.6% at a low potential of ~0.3 V<sub>RHE</sub>. This outperformed previous electrocatalysts measured under dark conditions. Theoretical calculation suggests that GaN NWs can convert NO<sub>3</sub>⁻ to the NO<sub>2</sub> key intermediate, which then interacts with a COO⁻ radical on the surface, coupling carbon and nitrogen as the initial crucial step for urea production. This circumvents the need for initial CO formation. Our findings reveal that GaN decorated with cocatalysts has high catalytic activity for C–N coupling, which is a key step in the production of fertilizers. This finding suggests that GaN could be used to develop more efficient and sustainable methods of producing fertilizers.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acscatal.3c04264.

Experimental methods, figures showing characterization data, and tables showing performance of photoelectrodes (PDF)

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Notes
The authors declare the following competing financial interest(s): Some IP related to this work was licensed to NS Nanotech, Inc. and NX Fuels, Inc., which were co-founded by Z. Mi. The University of Michigan and Mi have a financial interest in the companies.

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