ACS Energy LETTERS

Open Access
This article is licensed under CC-BY 4.0

pubs.acs.org/aelccp
Letter

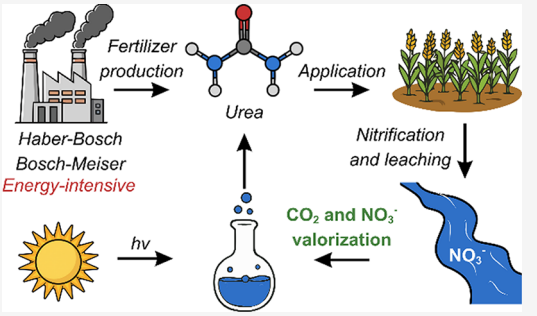
Valorization of Nitrate and Carbon Dioxide into Ammonia and Urea under Visible Light

Eve K Stegner, Nadeeka Lakshani, Madison R Kuns, Alba Ruiz-Aguirre, Ilaria Berruti, Sixto Malato, Gonzalo Guirado,* and Javier Vela*

Cite This: *ACS Energy Lett.* 2026, 11, 6651−6656
Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

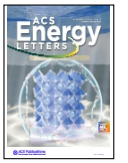
ABSTRACT: The energy-intensive manufacture of nitrogen-based fertilizers such as ammonia (NH_3) and urea consumes a significant fraction of the global energy supply. At the same time, widespread accumulation of excess nitrate (NO_3^-) from agricultural runoff poses serious risks to ecological and human health. These escalating environmental and economic costs highlight a pressing need for more sustainable fertilizer production. Photocatalytic conversion of waste NO_3^- into NH_3 underscores a growing interest in circular low-energy alternatives to the traditional Haber–Bosch process. For example, as the most widely applied nitrogen fertilizer, analogous routes to urea remain critically underdeveloped. We demonstrate the valorization of two abundant and harmful pollutants, nitrate and carbon dioxide (CO_2) into urea over a mixture of commercially available TiO_2 and CuO photocatalysts. The ability to drive this complex transformation under ambient temperature and pressure using solar energy highlights its potential to lower the energy demand of conventional fertilizer production. These results provide a fundamental platform from which to envision a more sustainable, visible light-driven ammonia/urea synthesis.



As the world's ever-rising consumption of resources intensifies pressure on agricultural feedstocks, the manufacture of nitrogen-based fertilizers is increasingly important.[1,2] Currently, well-established Haber–Bosch and Bosch–Meiser technologies are responsible for the commercial production of ammonia (NH_3) and urea (H_2NCONH_2), respectively.[3−5] These energy-intensive processes require operation temperatures reaching 200–500 °C and pressures often exceeding 15 MPa.[4,6] The combination of high energy reaction conditions paired with the growing need for synthetic nitrogen fertilizer results in NH_3 manufacture alone accounting for approximately 1–2% of global energy consumption along with the release of 235 million tons of CO_2 per year.[1,2,7,8] Interestingly, a large portion of carbon emissions are derived from the production of H_2—the precursor to ammonia—via steam methane reforming.[2,9] The colossal energy demands of fertilizer production translate directly into rising monetary costs, a trend further reflected in increasing prices of commercial NH_3 and urea.[10,11] Beyond its use in fertilizer, ammonia's growing appeal as an alternative fuel will push global demand even higher.[11,12] Further, excess ammonia and urea in agricultural soil undergo nitrification (to NO_3^-) and leaching into nearby surface water, which drive downstream ecological and human health risks (Figure 1). These processes collectively illustrate how current fertilizer production leads to long term impacts across atmospheric, human, and aquatic systems, stressing the need for alternative, circular pathways toward the synthesis and utilization of NH_3 and urea.

Addressing these growing concerns calls for developing chemical alternatives to recycle waste NO_3^- back into nitrogen-based fertilizers. For instance, photo- and electrocatalytic reduction is an emerging strategy for generating ammonia with minimal energy input while simultaneously remediating nitrate from waste streams and freshwater sources.[5,13−15] Nanostructured semiconductors show promise in the selective photocatalytic reduction of NO_3^- to NH_4^+ in acidic or neutral aqueous solutions under visible light,[5,13,16−18] and similar processes targeting urea are only beginning to emerge.[17,19−22] Developing low-energy pathways for valorization of NO_3^- into urea could be the key to mitigating the growing environmental impacts associated with nitrogen-based fertilizers.[23,24] Specifically, by redirecting waste streams into feedstocks to prepare ammonia and urea under mild conditions, this approach could substantially lower the energy associated with fertilizer and/or fuel production. In isolation,

Received: June 22, 2026
Revised: August 21, 2026
Accepted: August 31, 2026
Published: September 8, 2026



Downloaded from pubs.acs.org/aelccp/article-pdf/11/10/6651/6845427/nz-2026-01894h.pdf by guest on 28 October 2026

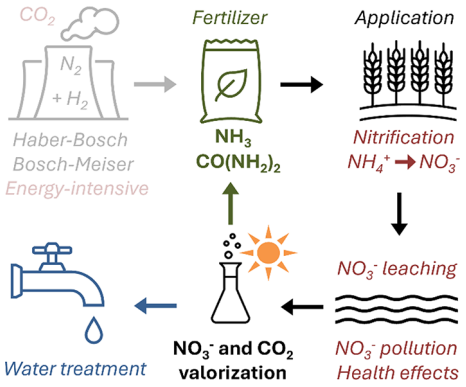


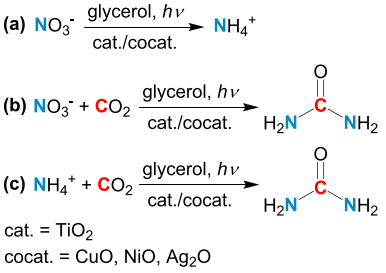
Figure 1. Photocatalytic valorization of NO_3^- and CO_2 from waste streams into NH_3 and urea.

photocatalytic NO_3^- or CO_2 reduction are each well-established.[5,13,14] These two fundamental reactions combined provide a route toward their valorization into urea and a possible alternative to the industrial Bosch–Meiser process. While several photo and electrocatalytic systems generate urea through reactions between NO_2^- or N_2 with CO or CO_2,[25,26] the reductive C–N coupling of NO_3^- and CO_2—two central targets for environmental remediation and resource recovery—remains challenging.[27−29] Initial reports reveal that photocatalysts utilized in the co-reduction of NO_3^- and CO_2 contain rare or multiple metal-based cocatalysts and semiconductors prepared via multistep synthetic procedures.[20−22] While these constructs promote efficient charge separation and improve activity,[20−22] they present challenges toward wide scale adoption and development due to the associated materials and fabrication. Thus, it is desirable to explore simpler and more earth-abundant photocatalysts for NO_3^- reduction to urea. Moreover, basic research into the reductive C–N coupling of NO_3^- and CO_2 under visible light could unveil the physical basis for strategic and sustainable N and C valorization.

Transition metal oxides exhibit well-established activity in catalytic NO_3^-[30,31] and CO_2 reduction,[32−35] making them attractive candidates for NO_3^- recovery and valorization into NH_4^+ and urea. Heterostructured metal oxides are particularly advantageous for pilot scale applications.[36] For instance, TiO_2 and Cu-based photocatalysts enable large scale photocatalytic water splitting.[36] Hand-ground mixtures of commercial TiO_2 and CuO nanocrystals spontaneously aggregate in aqueous solutions through electrostatic interactions arising from their opposing zeta potentials.[37,38] Inexpensive, readily accessible, and easy to prepare, the resulting TiO_2/CuO photocatalysts are ideal platforms to study the reductive coupling of NO_3^- with CO_2.

Remarkably, supplying a steady flow of CO_2 into 15 mL of an aqueous solution of ca. 1 mM NO_3^-, 10 mM glycerol, and 10 mg TiO_2/CuO photocatalyst under visible light results in the formation of both ammonia (NH_4^+ under neutral or acidic pH) and urea (Scheme 1 and Figure 2)—see Supporting Information. Mass spectra confirms the presence of urea, and reactions run with ^{15}N (*) isotopically labeled Na^*NO_3 generate labeled urea ($H_2{}^*NCO^*NH_2$), validating that nitrate is the source of nitrogen. Specifically, this TiO_2/CuO combination achieves 79% reduction of NO_3^-, and 250 μM of NH_4^+ and 20 μM of urea under 420 nm illumination in 24 h. Other cocatalysts such as NiO and Ag_2O show lower activity. Increasing the

Scheme 1. Photocatalytic Valorization of NO_3^- and CO_2 (10 mM Glycerol, 30 °C, 6–24 h, pH = 4).



initial concentration of NO_3^- from 1 mM to 4 mM increases the amount of urea from <10 μM to 30 μM after 6 h, and from 20 μM to 70 μM after 24 h. Starting with 4 mM nitrate, the yield of the reaction over TiO_2/CuO remains constant at 0.028 μg urea mg_{cat}^{-1} mL^{-1} h^{-1} between 6–12 h. Previous heterogeneous catalysts under comparable conditions reach yields of 0.108 μg urea mg_{cat}^{-1} mL^{-1} h^{-1} within 1 h, although this value reportedly decreases to 0.008 μg urea mg_{cat}^{-1} mL^{-1} h^{-1} within 3 h.[20] Thus, TiO_2/CuO displays more consistent rates of urea generation over extended periods of time. The combined selectivities for ammonium and urea remain less than 100% in most experiments. Additional analysis reveals little nitrite (<10 μM) is present after each experiment, suggesting a significant amount of nitrogen escapes in the form of nitrogen oxides and/or nitrogen gas, which can be common in nitrate reduction. Interestingly, a distinct fishy odor also suggests the generation of amines when reaction times exceed 12 h.[39] A comprehensive study of product identification and quantification will be the subject of a future paper. Apparent quantum yields (AQY) are 2.7% after 6 h and 1.2% after 24 h (Table 1). To test how ammonium concentration affects urea formation, we examined the coupling of NH_4^+ and CO_2 to urea over TiO_2/CuO. Indeed, urea forms faster starting with 2.5 mM solution of NH_4^+, reaching 40 μM in only 6 h.

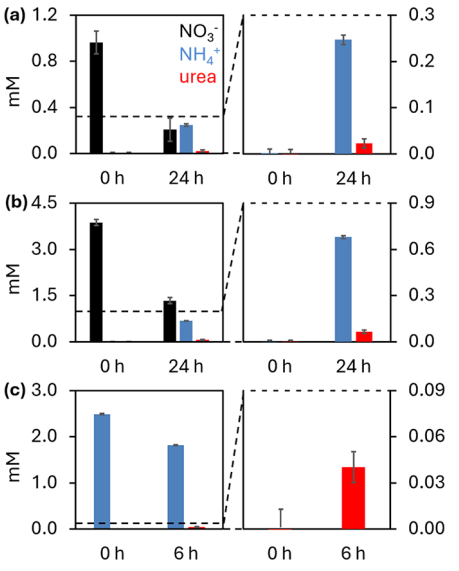


Figure 2. Photocatalytic valorization of NO_3^- (a, b) or NH_4^+ (c) with CO_2 into NH_4^+ and urea under 420 nm light (see Table 1).

Downloaded from pubs.acs.org/aelccp/article-pdf/11/10/6651/6845342/nz-2026-01894h.pdf by guest on 28 October 2026

https://doi.org/10.1021/acsenergylett.6c01894
ACS Energy Lett. 2026, 11, 6651−6656

Table 1. Photocatalytic Valorization of NO_3^- and CO_2 into NH_4^+ and Urea

reactant(s)[a]	photocat.	t (h)	λ (nm)	$[NO_3^-]$ (mM), conv. (%)[b]	$[NH_4^+]$ (μM)	[urea] (μM)	AQY (%)[c]
NO_3^- + CO_2	TiO_2/CuO	6	420	0.31, 35	230	<10	0.64
NO_3^- + CO_2	TiO_2/CuO	24	420	0.75, 79	250	20	0.32
4×NO_3^- + CO_2	TiO_2/CuO	6	420	1.47, 38	110	30	2.7
4×NO_3^- + CO_2	TiO_2/CuO	12	420	2.07, 53	210	60	1.9
4×NO_3^- + CO_2	TiO_2/CuO	24	420	2.54, 66	680	70	1.2
NO_3^- + CO_2[d]	TiO_2/CuO	6	420	0.16, 17	60	<10	0.3
2×NO_3^- + CO_2[e]	TiO_2/CuO	6	420	0.48, 27	150	<10	0.88
NO_3^- + HCO_3^- (0.1 M)	TiO_2/CuO	6	420	0.03, 2	<10	<10	0.08
NO_3^- + CO_2	TiO_2	6	420	0.20, 19	79	<10	0.44
NO_3^- + CO_2	CuO	6	420	0.00, <1	<10	<10	0
NH_4^+ (2.5 mM) + CO_2	TiO_2/CuO	6	420	- -	1820	40	-
2×NO_3^-[f]	TiO_2/CuO	6	420	1.51, 86	500	-	2.8
Raccoon River, 1.15 mM NO_3^- + CO_2	TiO_2/CuO	24	420	0.53, 46	260	20	0.25
Des Moines River, 0.42 mM NO_3^- + CO_2	TiO_2/CuO	24	420	0.19, 45	90	<10	0.09
Skunk River, 1.31 mM NO_3^- + CO_2	TiO_2/CuO	24	420	0.68, 52	450	20	0.32

[a]Initial $[NO_3^-]_\circ$ = 0.94–1.24 mM, 10 mg photocatalyst (10:1 $^w/_w$ TiO_2 to CuO), 15 mL solution, CO_2 supplied in excess into headspace (1 atm, 20 mL/min) unless otherwise indicated. [b]Uncertainties: $[NO_3^-]$ ± 0.10 mM, $[NH_4^+]$ ± 10 μM, [urea] ± 10 μM. [c]Determined from NO_3^- conversion; AQY (λ) (%) = 100 × number of reacted electrons / number of incident photons (see Supporting Information). [d]Sealed under static CO_2 atmosphere (1 atm, 0 mL/min). [e]Supplied in excess into solution (1 atm, 20 mL/min). [f]Reaction performed under the flow of Ar (1 atm, 20 mL/min).

To better understand the role of each metal oxide, we ran a series of control experiments and examined the effect of different experimental variables on NO_3^- conversion and the production of NH_4^+. Reactions run under 420 nm light in the absence of TiO_2 show that CuO alone is incapable of reducing NO_3^-. On the other hand, TiO_2 shows some NO_3^- reduction (19%) and 79 μM of NH_4^+. Because TiO_2 alone is unable to absorb 420 nm light, we attribute this marginal activity to residual electrons generated on the semiconductor surface under ambient light. (Storing TiO_2 in the dark for 48 h suppresses catalytic activity.[16]) These combined results indicate that CuO is necessary to build an active TiO_2/CuO photocatalyst capable of sustaining prolonged NO_3^- and CO_2 valorization to NH_4^+ and urea under visible light. Interestingly, previous reports show that CuO readily undergoes photoreduction to Cu_2O (and even Cu) in the presence of TiO_2, shifting the relative positions of the cocatalyst's conduction and valence bands[36,40,41] (or work function).[42,43] In other words, in situ reduction of the Cu-based cocatalyst may assist in the capture of visible photons and migration of photogenerated electrons to and from the conduction band of TiO_2, improving charge separation and promoting higher catalytic activity.

To gain additional physical insight into the reaction, we investigated the effect of CO_2 delivery on activity. A consistent flow of CO_2 (20 mL/min) through the headspace of the reaction results in the greatest activity. In contrast, sealing the reaction vessel and leaving it under static CO_2 (1 atm, 0 mL/min) slashes NO_3^- reduction from 35% to 17% and yield of NH_4^+ from 230 μM to 60 μM. A possible explanation may be the accumulation of O_2 gas from competing water oxidation in a closed system, which can inhibit nitrate reduction.[44] However, bubbling CO_2 directly (20 mL/min) into the solution rather than through the headspace causes a slight decrease in NO_3^- reduction from 35% to 27% and yield of NH_4^+ from 230 μM to 150 μM. Furthermore, replacing CO_2 with 100 mM HCO_3^- completely suppresses activity, showcasing that carbon dioxide delivery and speciation have significant effects on nitrate reduction. Finally, replacing CO_2 with Ar flow increases NO_3^- reduction from 35% to 86% and the yield of NH_4^+ from 230 μM to 500 μM. Because bubbling CO_2 normally reduces the pH of the solution from 5 to 4, and because acidification from 5 to 2 in the absence of CO_2 decreases nitrate reduction from 86% to 23% (see Supporting Information), we attribute this observation to a decrease of pH in the presence of dissolved carbonic acid. Critically, this also suggests that the source of carbon in urea is CO_2 rather than the sacrificial agent. Mass spectrometry further supports this deduction, as urea only appears as a product in the presence of CO_2. NO_3^- reduction ceases in the absence of glycerol. Photogenerated holes on the surface of the semiconductor oxidize glycerol, preventing charge carrier recombination, and supporting nitrate reduction.[45−48] ^{1}H NMR analysis indicates the formation of glycol-aldehyde and formic acid during the reaction (see Supporting Information). Together, these results reveal the essential role that the biomass-derived, hole-scavenging sacrificial agent plays in the valorization of NO_3^- and CO_2. Pushing this reaction to proceed with less glycerol and/or alternative electron donors may further lower the energy demand for nitrate and carbon dioxide valorization into urea.

Although TiO_2/CuO exhibits strong activity in controlled laboratory systems, its practical utility ultimately relies on their tolerance against contaminants found in natural waters. Environmental samples contain various types and amounts of organic matter, inorganic ions, and salinity which all vary greatly by region and can significantly influence catalytic activity. Because Iowa's robust agricultural productivity pushes substantial nutrient loading into its rivers, its waterways provide an environmentally significant platform for testing nitrate reduction catalysts under challenging, real-world conditions. Therefore, we collected raw water samples from three separate Iowa rivers to attain a more practical substrate for photocatalysis. Remarkably, TiO_2/CuO readily reduces nitrate to ammonia and urea in all three river samples in the presence of glycerol (Figure 3). Most impactful, nitrate levels in the Raccoon River and Skunk River dropped below the EPA limit of nitrate in water (0.7 mM) within 24 h under visible light.[49] These

Downloaded from pubs.acs.org/aelccp/article-pdf/11/10/6651/6845427/nz-2026-01894h.pdf by guest on 28 October 2026

https://doi.org/10.1021/acsenergylett.6c01894
ACS Energy Lett. 2026, 11, 6651−6656

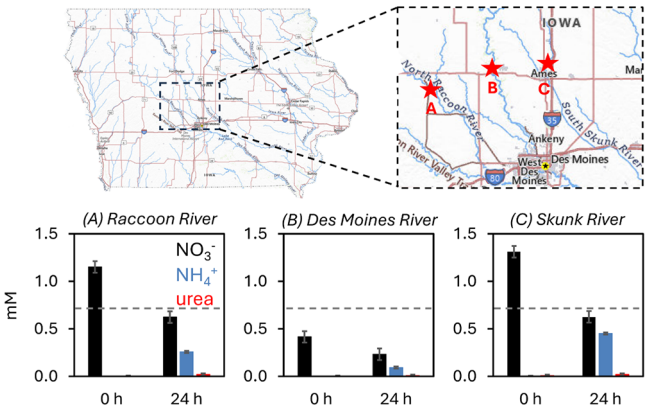


Figure 3. Photocatalytic nitrate reduction in water samples collected from the Raccoon River, Des Moines River, and Skunk River in Central Iowa (Summer 2026). The gray dashed line represents the EPA-recommended limit of nitrate in drinking water (0.7 mM).

findings showcase the outstanding resilience of these metal oxides to environmental contaminants, underscoring a critical need to devote further research into improving yield, product selectivity, and catalyst design.

In sum, we demonstrate the ability of CuO-modified TiO_2 in coupling nitrate reduction and carbon dioxide into urea. Our results showcase the effect of CO_2 source and mode of delivery—likely driven by competitive adsorption between CO_2 and NO_3^- on the catalyst surface—with the highest activity observed when CO_2 gas is continuously supplied to the headspace of the reaction. Maintaining a constant flow of CO_2 helps flush out adventitious oxygen and minimizes competition between oxygen and nitrate reduction. Glycerol plays an essential part as a sacrificial agent in supporting nitrate reduction. The conversion of nitrate and yield of ammonia are highest in the absence of CO_2; the lack of urea in this case indicates that the source of carbon is CO_2 rather than glycerol. Future work will address the photoinduced charge transfer, in situ Cu^{2+} reduction, and formation of carbon and nitrogen intermediates over TiO_2/CuO to guide fundamental improvements in yield and selectivity. Further development of these reactions may pave the way toward efficient valorization of NO_3^- and CO_2 into value-added products like ammonia and urea, lessening the energy demands and environmental impacts of conventional nitrogen-based fertilizers and fuels.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.6c01894.

Additional experimental details, photocatalysis results, mass spectra, and ^{1}H NMR (DOCX)

■ AUTHOR INFORMATION

Corresponding Authors

Gonzalo Guirado – *Departament de Química, Universitat Autonòma de Barcelona, Cerdanyola del Vallès, Barcelona 08193, Spain;* Email: Gonzalo.Guirado@uab.cat

Javier Vela – *Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States; US DOE Ames National Laboratory, Ames, Iowa 50011, United States;* orcid.org/0000-0001-5124-6893; Email: vela@iastate.edu

Authors

Eve K Stegner – *Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States*

Nadeeka Lakshani – *Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States*

Madison R Kuns – *Department of Chemistry, Iowa State University, Ames, Iowa 50011, United States*

Alba Ruiz-Aguirre – *CIEMAT – Plataforma Solar de Almería, Ctra. de Senés s/n, Tabernas, Almería 04200, Spain*

Ilaria Berruti – *Department of Chemistry and Physics, UAL, Ctra. de Sacramento s/n 04120, Almería*

Sixto Malato – *CIEMAT – Plataforma Solar de Almería, Ctra. de Senés s/n, Tabernas, Almería 04200, Spain*

Complete contact information is available at: https://pubs.acs.org/doi/10.1021/acsenergylett.6c01894

Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.V. thanks the U.S. National Science Foundation, Division of Chemistry, Macromolecular, Supramolecular, and Nanochemistry Program (2603808) for funding. A.R.-A., S.M.-R., and G.G. thank the European Union's Horizon Europe programme under grant agreement no. 101115182 (CONFETI—HORIZON-EIC-2022-PATHFINDERCHALLENGES-01) and UAB POC 2024 Programme (SUN4GREEN project) for financial support. I.B. thanks the Ministerio de Ciencia, Innovación y Universidades (MICIU/Agencia Estatal de Investigación (AEI)/10.13039/501100011033) for a Juan de la Cierva, JDC2023-052559-I grant and the European Social Fund Plus (ESF+). The authors thank Monica Haddad for assistance with ArcGIS.

■ REFERENCES

(1) Daramola, D. A.; Hatzell, M. C. Energy Demand of Nitrogen and Phosphorus Based Fertilizers and Approaches to Circularity. *ACS Energy Lett.* **2023**, *8*, 1493–1501.

(2) Lee, B.; Winter, L. R.; Lee, H.; Lim, D.; Lim, H.; Elimelech, M. Pathways to a Green Ammonia Future. *ACS Energy Lett.* **2022**, *7*, 3032–3038.

(3) Erisman, J. W.; Sutton, M. A.; Galloway, J.; Klimont, Z.; Winiwarter, W. How a Century of Ammonia Synthesis Changed the World. *Nat. Geosci.* **2008**, *1*, 636–639.

(4) Liu, L.; Zhou, L.; Zhang, L.; Huang, H.; Zhao, X.; Xu, Z. J. Green Urea Synthesis from CO_2 and Nitrogenous Small Molecules via Electrocatalysts and Photocatalysis. *Small Sci.* **2025**, *5*, No. 2500289.

(5) Ren, Z.; Shi, K.; Feng, X. Elucidating the Intrinsic Activity and Selectivity of Cu for Nitrate Electroreduction. *ACS Energy Lett.* **2023**, *8*, 3658–3665.

(6) Xiong, Y.; Wang, Y.; Zhou, J.; Liu, F.; Hao, F.; Fan, Z. Electrochemical Nitrate Reduction: Ammonia Synthesis and the Beyond. *Adv. Mater.* **2024**, *36*, No. 2304021.

Downloaded from pubs.acs.org/aelccp/article-pdf/11/10/6651/6845427/nz-2026-01894h.pdf by guest on 28 October 2026

(7) The Royal Society. In Ammonia: Zero-carbon Fertiliser, *Fuel and Energy Store*, **2026**. https://royalsociety.org/green-ammonia (accessed April 24th, 2026).
(8) International Energy Agency. In *Ammonia Technology Roadmap: Towards More Sustainable Nitrogen Fertiliser Production*, OECD Publishing: Paris; **2021**. https://www.iea.org/reports/ammonia-technology-roadmap (accessed April 24th, 2026).
(9) Hatzell, M. C. The Colors of Ammonia. *ACS Energy Lett.* **2024**, *9*, 2920–2921.
(10) Yang, M.; Wang, X.; Fathololoumi, S.; Vasava, H. B.; Zhou, Y.; Chau, H. W.; Li, H.; Si, B.; Li, H.; Biswas, A. How Fertilizer Shortages Caused by the Energy Crisis Threaten Food Security. *Nature* **2026**, *653*, 26–29.
(11) Tan, H.; Sang, Z.; Tian, Y.; Peng, W.; Liu, X.; Liang, J. Ammonia as a Green Carbon-Free Fuel: A Pathway to the Sustainable Energy Economy. *ACS Energy Lett.* **2024**, *9*, 5120–5136.
(12) Boretti, A.; Castelletto, S. NH_3 Prospects in Combustion Engines and Fuel Cells for Commercial Aviation by 2030. *ACS Energy Lett.* **2022**, *7*, 2557–2564.
(13) Youn, G.; Hong, I.; Song, B.; Lee, D.; Yun, Y.; Moon, H, S.; Yong, K. Present State and Future Outlook of Ammonia Production through Photocatalytic Nitrate Reduction. *Sol. RRL* **2024**, *8*, No. 2300880.
(14) Zhang, C.; Li, J.; Chen, R.; Shen, S.; Wang, J.; Sun, Y.; Song, F. NH_3 Synthesis from N_1 Compounds by Photocatalytic Technology: Promotion Mechanism, Reaction Pathways, and Efficiency Evaluation Criteria. *ACS Catal.* **2024**, *14*, 15721–15742.
(15) Goyal, I.; Qi, Y.; Singh, M. R. Toward a Distributed Nitrate Economy. *Ind. Eng. Chem. Res.* **2025**, *64*, 14789–14801.
(16) Wei, L.; Adamson, M. A.; Vela, J. Ni_2P-Modified Ta_3N_5 and TaON for Photocatalytic Nitrate Reduction. *ChemNanoMat* **2020**, *6*, 1179–1185.
(17) Bhattacharyya, B.; Sarhan, R. M.; Lu, Y.; Taubert, A. A Perspective on Photocatalytic Synthesis of NH_3, Urea, and Amino Acids by Nanomaterials: Progress and Prospects. *ChemCatChem* **2024**, *16*, No. e202400638.
(18) Wang, C.; Luo, Y.; Liu, J.; Zhu, R.; Zhao, P.; Fu, L.; Vela, J.; Fan, H.-J. S. Advances and Mechanistic Studies of Cu-Based Heterostructures for Nitrate Reduction. *Inorg. Chem.* **2025**, *64*, 16277–16288.
(19) Yang, Z.; Li, P. Research Progress in Photochemical Synthesis of Urea through C–N Coupling Reactions. *RSC Adv.* **2025**, *15*, 48775–48794.
(20) Sun, H.; Lin, Z.; Tang, R.; Liang, Y.; Zou, S.; Zhang, X.; Chen, K.; Zheng, R.; Huang, J. Enhanced Solar Urea Synthesis from CO_2 and Nitrate Waste via Oxygen Vacancy Mediated-TiO_x Support Lead-free Perovskite. *Appl. Catal. B* **2025**, *360*, No. 124511.
(21) Lou, Z.; Zhong, Q.; Xu, H.; Liu, Y.; Liu, K.; Yuan, W.; Kang, K.; Liu, G.; Liu, J.; Yu, S.; Bao, Y. In Situ Construction of CuS/NiS/Ti_3C_2 Heterojunction for Efficient Photocatalytic Urea Synthesis from CO_2 and Nitrate. *Sep. Purif. Technol.* **2026**, *395*, No. 137684.
(22) Bao, T.; Tang, C.; Wu, Y.; Bi, Y.; Zhang, C.; Xi, Y.; Zou, Y.; Liu, C.; Yu, C. Photocatalytic Co-Reduction of CO_2 and Nitrate over Porphyrin Metal-Organic Frameworks: Dual Atomic Active Site and Nanostructure Synergy Enhances C–N Coupling for Urea Production. *Angew. Chem., Int. Ed.* **2025**, *64*, No. e202512615.
(23) Muhyuddin, M.; Zuccante, G.; Mustarelli, P.; Filippi, J.; Lavacchi, A.; Elbaz, L.; Chen, Y.-H.; Atanassov, P.; Santoro, C. Electrochemical Urea Production using Carbon Dioxide and Nitrate: State of the Art and Perspectives. *Energy Environ. Sci.* **2024**, *17*, 3739–3752.
(24) *Ammonia Technology Roadmap*, IEA: Paris; **2021** https://www.iea.org/reports/ammonia-technology-roadmap.
(25) Han, C.; Wang, K. Recent Advances in Photoelectrochemical Synthesis of Nitrogen-Containing Solar Fuels and Chemicals. *Energy Fuels* **2025**, *39*, 16065–16077.
(26) Xie, F.; Wu, Z.; Yang, J. Valorizing Nitrate in Electrochemical Nitrogen Cycling: Copper-Based Catalysts from Reduction to C–N Coupling. *Small* **2025**, *21*, No. 2500833.
(27) Liang, H.; Li, M.; Li, Z.; Liu, X.; Xu, X.; Yu, S.; Xie, W.; Zhang, T.; Duan, H.; Wang, Q. Ternary Facet Junction Engineered Cu_2O Photocathode for Efficient Urea Synthesis via CO_2 and NO_3^- Co-reduction. *ACS Energy Lett.* **2026**, *11*, 3853–3860.
(28) Wang, F.; Shang, S.; Li, Z.; Zhang, Z.; Chu, K. Selective Urea Electrosynthesis from Nitrate and CO_2 on Isolated Copper Alloyed Ruthenium. *ACS Energy Lett.* **2024**, *9*, 4624–4632.
(29) Song, H.; Haro, D.-C.; Huang, P.-W.; Barrera, L.; Hatzell, M. C. Progress in Photochemical and Electrochemical C–N Bond Formation for Urea Synthesis. *Acc. Chem. Res.* **2023**, *56*, 2944–2953.
(30) Zhao, X.; Zhang, G.; Zhang, Z. TiO_2-based Catalysts for Photocatalytic Reduction of Aqueous Oxyanions: State-of-the-art and Future Prospects. *Environ. Int.* **2020**, *136*, No. 105453.
(31) Zhou, J.; Gao, S.; Hu, G. Recent Progress and Perspectives on Transition Metal-Based Electrocatalysts for Efficient Nitrate Reduction. *Energy Fuels* **2024**, *38*, 6701–6722.
(32) Du, Y.; Tang, Y.-T.; Ma, X.; Li, J.; Guo, Q. Design, Synthesis, and Diverse Applications of Cu-Based Photocatalysts: A Review. *Cryst. Growth Des.* **2024**, *24*, 2592–2618.
(33) Zhong, K.; Sun, P.; Xu, H. Advances in Defect Engineering of Metal Oxides for Photocatalytic CO_2 Reduction. *Small* **2025**, *21*, No. 2310677.
(34) Dang, H.; Guan, B.; Chen, J.; Ma, Z.; Chen, Y.; Zhang, Y.; Guo, Z.; Chen, L.; Hu, J.; Yi, C.; Yao, S.; Huang, Z. Research Status, Challenges, and Future Prospects of Carbon Dioxide Reduction Technology. *Energy Fuels* **2024**, *38*, 4836–4880.
(35) Guo, R.; Guo, S.; Yu, L.; Pan, W. Recent Progress and Perspectives of S-Scheme Heterojunction Photocatalysts for Photocatalytic CO_2 Reduction. *Energy Fuels* **2024**, *38*, 869–894.
(36) Ruiz-Aguirre, A.; Villachica-Llamosas, J. G.; Polo-López, M. I.; Cabrera-Reina, A.; Colón, G.; Peral, J.; Malato, S. Assessment of Pilot-Plant Scale Solar Photocatalytic Hydrogen Generation with Multiple Approaches: Valorization, Water Decontamination and Disinfection. *Energy* **2022**, *260*, No. 125199.
(37) Kum, J. M.; Yoo, S. H.; Ali, G.; Cho, S. O. Photocatalytic Hydrogen Production over CuO and TiO_2 Nanoparticles Mixture. *Int. J. Hydrogen Energy*, **2013**, *38*, 13541–13546.
(38) Stegner, E. K.; Kuns, M. R.; Ochoa-Romero, K.; Guirado, G.; Vela, J. Ball Mill Beatdown: Mechanochemical Synthesis of TaON Nanocrystals. *Inorg. Chem.* **2026**, *65*, 11827–11835.
(39) Kumawat, S.; Singh, S.; Bhatt, T.; Maurya, A.; Vaidyanathan, S.; Natte, K.; Jagadeesh, R. V. Valorization of Bio-renewable Glycerol by Catalytic Amination Reactions. *Green Chem.* **2024**, *26*, 3021–3038.
(40) Maldonado, M. I.; Saggioro, E.; Peral, J.; Rodríguez-Castellón, E.; Jiménez-Jiménez, J.; Malato, S. Hydrogen Generation by Irradiation of Commercial CuO + TiO_2 Mixtures at Solar Pilot Plant Scale and in Presence of Organic Electron Donors. *Appl. Catal. B* **2019**, *257*, No. 117890.
(41) Toe, C. Y.; Zheng, Z.; Wu, H.; Scott, J.; Amal, R.; Ng, Y. H. Photocorrosion of Cuprous Oxide in Hydrogen Production: Rationalizing Self-Oxidation or Self-Reduction. *Angew. Chem. Int. Ed.* **2018**, *57*, 13613–13617.
(42) Rej, S.; Bisetto, M.; Naldoni, A.; Fornasiero, P. Well-defined Cu_2O Photocatalysts for Solar Fuels and Chemicals. *J. Mater. Chem. A* **2021**, *9*, 5915–5951.
(43) Zhang, Y.-H.; Liu, M.-M.; Chen, J.-L.; Fang, S.-M.; Zhou, P.-P. Recent Advances in Cu_2O-based Composites for Photocatalysis: A Review. *Dalton Trans.* **2021**, *50*, 4091–4111.
(44) Bie, C.; Wang, L.; Yu, J. Challenges for Photocatalytic Overall Water Splitting. *Chem* **2022**, *8*, 1567–1574.
(45) Kormányos, A.; Szirmai, A.; Endrődi, B.; Janáky, C. Pairing Electrochemical CO_2 Reduction with Glycerol Oxidation: Bottlenecks Today, Opportunities Tomorrow. *Joule*, **2025**, *9*, No. 102096.
(46) Ebeling, K. M.; Bongartz, D.; Mürtz, S.; Palkovits, R.; Mitsos, A. Thermodynamic and Economic Potential of Glycerol Oxidation to Replace Oxygen Evolution in Water Electrolysis. *Ind. Eng. Chem. Res.* **2024**, *63*, 8250–8260.
(47) Aguirre, A. R.; Reina, A. C.; Pérez, J. P.; Colon, G.; Malato, S. Catalysts and Photoreactors for Photocatalytic Solar Hydrogen Production: Fundamentals and Recent Developments at Pilot Scale.

Downloaded from pubs.acs.org/aelccp/article-pdf/11/10/6651/6845427/nz-2026-01894h.pdf by guest on 28 October 2026

https://doi.org/10.1021/acsenergylett.6c01894
ACS Energy Lett. 2026, 11, 6651–6656

In *Photocatalytic Hydrogen Production for Sustainable Energy [Online]* Ed., Puga, A., **2023**; pp 275–317. https://onlinelibrary.wiley.com/doi/10.1002/9783527835423.ch12 (accessed 8-20-2023).

(48) Reddy, N. L.; Cheralathan, K. K.; Kumari, V. D.; Neppolian, B.; Venkatakrishnan, S. M. Photocatalytic Reforming of Biomass Derived Crude Glycerol in Water: A Sustainable Approach for Improved Hydrogen Generation Using $Ni(OH)_2$ Decorated TiO_2 Nanotubes under Solar Light Irradiation. *ACS Sustainable Chem. Eng.* **2018**, *6*, 3754–3764.

(49) National Primary Drinking Water Regulations. In *EPA-F-09-004*, United States Environmental Protection Agency: Washington, DC; **2009**.

Downloaded from pubs.acs.org/aelccp/article-pdf/11/10/6651/6845427/nz-2026-01894h.pdf by guest on 28 October 2026

https://doi.org/10.1021/acsenergylett.6c01894
ACS Energy Lett. 2026, 11, 6651–6656