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Solar Urea: Towards a Sustainable Fertilizer Industry

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Abstract: Urea, an agricultural fertilizer, nourishes humanity. The century-old Bosch-Meiser process provides the world's urea. It is multi-step, consumes enormous amounts of non-renewable energy, and has a large CO₂ footprint. An eco-friendly synthesis for urea is a priority. Herein we report a single-step Pd/LTA-3A catalyzed synthesis of urea from CO₂ and NH₃ under ambient conditions, powered solely by solar energy. Pd nanoparticles serve the dual function of catalyzing the dissociation of NH₃ and providing the photothermal driving force for urea formation, while the absorption capacity of LTA-3A removes by-product H₂O, shifting the equilibrium towards urea production. The solar urea conversion rate from NH₃ and CO₂ is 87 μmol g⁻¹ h⁻¹. This advance represents a first step towards the use of solar energy in urea production. It provides insights into green fertilizer production, and inspires the vision of sustainable, modular plants for distributed production of urea on farms.

Humans and animals excrete excess nitrogen in the form of urea. Historically, urea was the first naturally occurring organic compound to be synthesized by Friedrich Wöhler in 1828. Surprisingly at the time, he made all-organic urea by a thermally induced reconstruction of an all-inorganic compound, ammonium cyanate, connecting the fields of organic and inorganic chemistry. Since that time urea has become one of the most indispensable chemicals to society as a nitrogen-based fertilizer. In 2020, the global demand for urea reached 187.8 million metric tons, and is expected to grow at 2% per annum reaching 211.5 million metric tons by 2026, with approximately 80% of the demand projected for fertilizer usage.^[1] Having higher nitrogen content and lower transport cost compared to other common nitrogenous fertilizers, urea accounts for more than 50% of the total consumption of nitrogen fertilizer.^[2] Since more than 40% of the world's food production relies on fertilizers and the global population is predicted to reach 9.7 billion in 2050, the demand for urea is anticipated to remain high for decades.^[3] In addition to fertilizer, urea is an important feedstock for the chemical industry, mainly for the synthesis of plastics, urea-formaldehyde resins and adhesives, and animal feed.^[4]

Currently, the predominant method for the industrial production of urea is the Bosch-Meiser process, first developed in 1922. This century-old process contains two steps: (i) liquid ammonia (NH₃) reacts with gaseous carbon dioxide (CO₂) to form ammonium carbamate followed by (ii), ammonium carbamate decomposes into urea and water. Due to the requirement of high temperature (above 180 °C) and pressure (around 150 bar), this process is energy-intensive and produces vast quantities of CO₂ emissions. About 21-29 billion million kilojoules of energy are consumed and 0.7-2.3 tons of CO₂ are emitted per ton equivalent of urea produced.^[5] There exist only few reports of urea synthesis under ambient conditions, using plasma and electrochemical techniques, yet none exploiting the use of light. Briefly, Xiang *et al.* reported that urea can be synthesized by gaseous negative corona discharges, and Yahya *et al.* studied urea formation catalyzed by magnetite subjected to magnetic fields.^[6] Electrochemical synthesis of urea has been explored recently as well. Chen *et al.* reported PdCu alloy nanoparticles on TiO₂ nanosheets could produce urea from N₂ and CO₂ with a Faradic efficiency of 8.92%.^[7] Feng *et al.* demonstrated Te-doped Pd nanocrystals promoted urea synthesis by coupling CO₂RR with electrochemical reduction of nitrite.^[8] Yuan *et al.* found a novel Mott-Schottky Bi-BiVO₄ heterostructures-enabled urea synthesis from N₂ and CO₂, with a Faradaic efficiency increased to 12.55%.^[9] **However, to the best of our knowledge, no reports currently exist utilizing solar energy for urea synthesis to reduce the intensity of its operating conditions.**

Herein we report a green chemistry approach for producing solar urea from the reaction of NH₃ and CO₂ enabled by a hybrid photocatalyst: palladium nanoparticles loaded on molecular sieve LTA-3A, denoted as Pd/LTA-3A. The Pd nanoparticles catalyze the dissociative adsorption of NH₃ to Pd-NH₂ and Pd-H surface species, which react with CO₂ to form urea.^[10] In addition, the Pd nanoparticles can act as nanoscale heaters to accelerate the reaction by the photothermal effect, originating from plasmonic and non-radiative relaxation of photo excited charge carriers.^[11] Furthermore, the high H₂O absorption capacity of LTA-3A drives the reaction equilibrium towards urea formation by removal of H₂O,

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the by-product.^[12] In addition, the LTA-3A functions as a stabilizing support to minimize the aggregation and sintering of Pd nanoparticles. With photo irradiation as the only source of energy, Pd/LTA-3A catalyzes urea formation from NH_3 and CO_2 under ambient temperature and pressure conditions. We envision this as a step towards sustainable, modular plants for the distributed production of solar urea on farms.

Pd/LTA-3A was obtained via a microwave-assisted solvothermal process. With ethanol acting as the reducing agent, the Pd nanoparticles were formed and deposited on the surface of LTA-3A, as shown in the **Figure 1a, 1b, S1 and S2** by environmental scanning electron microscopy (ESEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM). The size distribution of the Pd nanoparticles is broad ranging from 2 to 300 nm (**Figure S1-S3**). The Pd loading of Pd/LTA-3A is 0.036%, determined by inductively coupled plasma-atomic emission spectrometry (ICP-AES).

Figure 1. Characterization of Pd/LTA-3A. (a) Schematic illustration of Pd/LTA-3A synthesis. (b) ESEM (left) and HAADF-STEM (right) images of Pd/LTA-3A. (c) HRTEM image and FFT pattern of Pd nanoparticles. Scale bar: 5 nm. (d) TEM image (left), the EELS analysed region is marked by the rectangle; and EELS mapping images of Pd and O (right). Scale bar: 50 nm.

Electron energy loss spectroscopy (EELS), high-resolution transmission electron microscopy (HRTEM) and powder X-ray diffraction (XRD) were performed to characterize the nature of the Pd nanoparticles. In the XRD patterns, a peak of Pd{111} was clearly shown after the introduction of Pd on LTA-3A (**Figure S4**), indicating the existence of Pd metal.^[13] The {111} facet was also observed in the HRTEM images (**Figure 1c**), confirming that the nanoparticles are Pd(0). To conduct a more rigorous investigation on the Pd oxidation state, EELS was performed on the samples synthesized via the same method in the absence of LTA-3A, to

avoid interference from LTA. As shown in **Figure 1d** and **Figure S5**, the large-area EELS mapping of elemental Pd fits well with the shape of particle with negligible signal from O, indicating the metallic zero valence nature of the Pd nanoparticles.

The optical absorbance of Pd/LTA-3A was investigated by ultraviolet-visible-near infrared (UV-VIS-NIR) spectroscopy (**Figure S6**). Plasmon, inter-band and intra-band electronic transitions in Pd nanoparticles contribute to optical absorption in the range 200–850 nm for sizes in the range of 2–300 nm.^[11d, 13] In our case, due to the wide size distribution of Pd nanoparticles, the UV-VIS-NIR spectra showed intense broadband absorption over the entire 200–1000 nm wavelength range, much higher than LTA-3A alone which absorbs in the UV.

We studied the reactivation of the catalyst to ensure the suitability of the nanoparticle support, LTA-3A, a molecular sieve, that was chosen to absorb water produced during reaction. Thermal gravimetric analysis (TGA) was performed to study the dehydration of the Pd/LTA-3A catalyst (**Figure S7**). For the completely saturated sample, it lost approximately 30%, 50% and 90% of the absorbed water at 100 °C, 120 °C and 180 °C, respectively. Therefore, the reactivation of Pd/LTA-3A can be conducted under relatively mild conditions that will not cause the sintering of Pd nanoparticles.

The catalyst performance was tested in a batch reactor with a quartz window irradiated by a 300 W Xe lamp (**Figure S8**). NH_3 and CO_2 were inputted with the ratio of 2:1, and the overall pressure was set as 1 atm. The catalysts were all pre-treated at 120 °C under vacuum for 30 min before adding reactant gases to eliminate interference of pre-absorbed H_2O in LTA-3A. Nuclear magnetic resonance (NMR) and liquid chromatography–mass spectrometry (LC-MS) were performed to analyze the product of the reaction to confirm the formation of urea and quantify the amount. Using a modified method based on literature, we performed LC-MS and assigned the peaks of $m/z = 61$ and 44 at 3–4 min to protonated urea and its fragment, cyanic acid.^[14] The concentration of urea in the extracted solution from the reactor was determined using a calibration curve for a series of urea standard solutions. Within a certain range, the peak area obtained from LC-MS has a linear relationship with the concentration (**Figure S9**).

Figure 2. Superimposed extracted-ion chromatogram (EIC) of LC-MS spectra of solution collected after a typical test catalysed by Pd/LTA-3A using (a) $^{14}\text{NH}_3 + ^{12}\text{CO}_2$, (b) $^{15}\text{NH}_3 + ^{12}\text{CO}_2$, and (c) $^{14}\text{NH}_3 + ^{13}\text{CO}_2$. Red and black lines represent the protonated positive ion (inset) and fragment of urea, respectively. ^1H NMR spectra of solution collected after a typical test catalysed by Pd/LTA-3A using CO_2 and (d) $^{14}\text{NH}_3$, (e) $^{15}\text{NH}_3$.

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In a blank control test, with the absence of any catalyst, no detectable amount of urea was formed when the reactor was heated to reach 80 °C, 100 °C, 120 °C or 150 °C. The performance of Pd/LTA-3A was tested with the same gas composition and pressure, only difference being the energy source, as the reactor was not heated; the irradiance from the lamp was the only energy source. The illumination intensity was 4.9 suns, measured by a light meter. Under such light intensity, in the blank reactor, the apparent temperature detected by the thermocouple inside the reactor was 47 °C. In the catalyst performance tests, due to the photothermal effect of Pd nanoparticles, the apparent temperature reached 100 °C under illumination. At 1 atm, the decomposition temperature of ammonium carbamate, the key chemical involved in the Bosch-Meiser process, is around 60 °C. Therefore, in our case, ammonium carbamate was unstable, which was different from that in industrial ammonia production. Both the EIC of LC-MS and NMR ^1H spectrum confirmed the formation of urea (Figure 2a, 2d and S10). The activity of Pd/LTA-3A under light was $87\ \mu\text{mol g}_{\text{Pd}}^{-1}\text{ h}^{-1}$ or $31\ \text{nmol g}_{\text{catalyst}}^{-1}\text{ h}^{-1}$. Furthermore, to confirm the nitrogen and carbon origin of the urea, the same tests using isotopically ^{15}N labeled $^{15}\text{NH}_3$ and ^{13}C labeled $^{13}\text{CO}_2$ were performed. The peaks of $m/z = 63$ (protonated positive ^{15}N -urea ion) and 45 (^{15}N -urea fragment) appeared in LC-MS for a $^{12}\text{CO}_2 + ^{15}\text{NH}_3$ test, with the doublet shown in the ^1H NMR.^[15] No such peaks could be observed for pure water or ^{14}N , ^{12}C -urea (Figure 2b-2e and S11). In a $^{13}\text{CO}_2 + ^{14}\text{NH}_3$ test, $m/z = 62$ and 45 were detected via the LC-MS. These results confirmed that urea was formed by the reaction between NH_3 and CO_2 . **To the best of our knowledge, this is the first time that solar urea has been synthesized under ambient temperature and pressure conditions.**

Figure 3. Catalytic performance for urea synthesis. (a) Urea production rates under different conditions. (b) Arrhenius plots of $\ln(\text{urea production rate})$ and $1000/\text{temperature}$ of Pd/LTA-3A tested in the light and dark. (c) Stability of Pd/LTA-3A performance for urea production.

The indispensability of both Pd and LTA-3A for solar urea synthesis was proven by control tests. Pd has been reported as a catalyst for ammonia dissociation and exhibits the photothermal effect.^[10-11] As seen from Figure 3a, in the absence of Pd nanoparticles, the pure LTA-3A demonstrated no urea production. A control Pd/SiO₂ sample prepared via the same microwave-assisted solvothermal method to Pd/LTA-3A (Figure S12),

showed urea production of $66\ \mu\text{mol g}^{-1}\text{ h}^{-1}$, 75% that of the Pd/LTA-3A. These results highlighted the Pd as active center which can be promoted by the LTA-3A.

In our design, the essential promotion effect of LTA-3A should originate from the thermodynamic driven force of moving the $2\text{NH}_3 + \text{CO}_2 = \text{CO}(\text{NH}_2)_2 + \text{H}_2\text{O}$ reaction forward via the Le Chatelier principle, since the LTA-3A is a well-known desiccant. To support this hypothesis, control tests were designed by eliminating the thermal pretreatment step (in vacuum) of the catalyst before the input of reactant gases, which allowed the LTA-3A to be pre-saturated with water as indicated by TGA (Figure S13). As shown in Figure 3a, the urea production rate of unpreheated Pd/LTA-3A is 43% lower than that of preheated Pd/LTA-3A, confirming that the water trap capability of LTA-3A favors urea formation during the reaction.

To study the effect of light, control tests were conducted under the dark condition. In the standard test, the photothermal effect of Pd nanoparticles can increase the apparent temperature to 100 °C under light irradiation. Therefore, for the dark tests, external heat was provided to maintain a same apparent temperature. As shown in Figure 3a, urea formation over Pd/LTA-3A could increase 3.2 times under light ($87\ \mu\text{mol g}^{-1}\text{ h}^{-1}$) compared to the $27\ \mu\text{mol g}^{-1}\text{ h}^{-1}$ in the dark. The conversion of reactants in 15 min increased to 0.004%. To determine the activation energy, a series of tests with different temperatures were performed. By adjusting the external heat for dark tests and the distance of the solar lamp to reactor for light tests, urea production rates with different temperature are shown in Figure 3b. The activation energies for urea synthesis in the dark and light conditions were calculated to be $75.5\ \text{kJ mol}^{-1}$ and $74.1\ \text{kJ mol}^{-1}$, respectively. Such a minor difference indicates the reaction mechanism under illumination is similar to that in the dark condition. The local temperature of the active site under illumination for urea synthesis is estimated from the conversion to be 111 °C.

The stability of Pd/LTA-3A's catalytic performance was further investigated by reusing the same catalyst for 5 runs under the standard test condition. Figure 3c showed that the activity of the catalyst did not noticeably change. In addition, ESEM and XRD established the size, morphology, and oxidation state of the Pd nanoparticles remained essentially the same after 5 runs (Figure S3, S4).

Figure 4. *In situ* DRIFTS spectra of Pd/LTA-3A surface. Condition: 4 sccm NH₃, 2 sccm CO₂ and 10 sccm He, 100 °C, dark. (a) 3800-2400 cm⁻¹ region. (b) 1800-1200 cm⁻¹ region.

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In situ diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) in the dark was performed to probe the species on the catalyst surface. With a slow flow of NH_3 , CO_2 and Ar, the DRIFTS spectra obtained are shown in **Figure 4**. In the spectra, the two sharp doublets appeared between 3750 cm^{-1} and 3580 cm^{-1} are attributed to CO_2 . The NH_3 N-H stretching peaks are observed at 3375 and 3245 cm^{-1} , while those of NH_{1-2} locate at $2400\text{--}3122\text{ cm}^{-1}$, with corresponding peak overlapped with the negative C-H bands at 2965 and 2878 cm^{-1} which typically originate from residual organic compounds. The NH_{1-2} are believed to result from partial ammonia decomposition with the formation of Pd-H species. This reaction scheme is supported by the emerging $(\text{H}_2)_y\text{PdH}$ (1829 and 1871 cm^{-1}) and PdH_2 (1260 cm^{-1}) peaks during ammonia decomposition over illuminated Pd/LTA-3A (**Figure S14**). The byproduct water induced broad O-H stretching peak was observed in the 2700 to 3700 cm^{-1} region. The

bending modes of these high-wavenumber stretching bands emerged in the range of $1200\text{--}1800\text{ cm}^{-1}$. To amplify, peaks at 1585 cm^{-1} and 1460 cm^{-1} can be assigned to N-H bending modes, where the former band has a slight overlap with the COO^- stretching band around 1560 cm^{-1} . The typical water-related O-H scissors are observed at 1625 cm^{-1} . Peaks centered at 1680 cm^{-1} and 1400 cm^{-1} are attributed to C=O and C-N stretching modes, respectively. The peak at 1300 cm^{-1} is assigned to the skeletal vibration of NCOO^- .^[16] These peaks grow as NH_3 and CO_2 continuously flowing through the chamber, indicating an increase in species amount. As discussed above, the comparable activation energies of dark and light tests indicate the reaction pathway should be similar, which is verified by DRIFTS experiment in the light. As shown in the **Figure S15**, under the irradiation, the surface species are the same as in the dark condition.

Figure 5. Reaction pathway studies of urea formation from CO_2 and NH_3 catalysed by Pd/LTA-3A. (a) Three simplified routes to urea formation. (b) Top-view and side-view configurations of (i) $2\text{NH}_3\text{-CO}_2$ route, (ii, iv) $2\text{NH}_2\text{-2H-CO}_2$ route, and (iii, v) 2NH-4H-CO_2 route based on DFT calculation. Routes i, ii and iii occurred on Pd(111) facet while iv and v were on Pd step sites. (c) Calculated energy diagram of the five routes, and * represents the absorbed state.

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Based on the DRIFTS data shown in **Figure 4**, **S14** and **S15**, three potential reaction pathways involving PdH_x, NH, NH₂, NH₃, CO₂, and NCOO intermediates for urea formation can be proposed, as illustrated in **Figure 5**. (1) The direct reaction of NH₃ and CO₂ to form urea, which contains two steps: the adsorbed NH₃ and CO₂ form H₂O and NH₂CONH₂ (II), followed by the desorption of urea from the surface of catalyst. (2) Dissociative adsorption of NH₃ on the surface of the Pd nanoparticles produces amine (Pd-NH₂) and hydrogen (Pd-H) species in the first step. Then the nucleophilic addition between Pd-NH₂ and CO₂ results in the formation of a carbamate intermediate (II'). The neighboring Pd-H and NH₂ from carbamate react with oxygen, resulting in the formation of NHCO and H₂O which later desorbed from the Pd surface (IV', V') and accumulated on the LTA-3A. The second nucleophilic addition reaction between Pd-NH₂ and NHCO lead to the formation of NHCONH₂ (VI'), which subsequently reacts with nearby Pd-H, eventually forming urea (VII'). (3) Pd catalyzes the dissociation of NH₂ to NH and H. The first nucleophilic addition between NH and CO₂, together with the reaction between Pd-H and oxygen, generates H₂O and NHCO (II'', III''). H₂O is absorbed by LTA-3A and NHCO reacts with NH and Pd-H to produce urea (IV''). Above reaction schemes are on the Pd(111) surface, while those on Pd step sites are also possible considering the step-rich ultrafine Pd nanoparticles in our Pd/LTA-3A catalyst (**Figure 5b**, iv and v).

Catalyst structure-based density functional theory (DFT) calculations were employed to further study the feasibility of the five routes. First, to understand the origin of NH and NH₂ intermediates, the NH₃-Pd interaction was computed (**Figure S16** and **S17**). The heat released from NH₃ absorption [-3.34 and -4.21 eV on Pd(111) and Pd steps, respectively] are large enough to compensate the energy required to convert NH₃ to NH₂-H [1.66 and 1.68 eV on Pd(111) and Pd steps, respectively] and further to NH-2H [1.65 and 2.67 eV on Pd(111) and Pd steps, respectively]. This result suggests the NH₃ readily decomposes on contact with Pd. Subsequent reactions on Pd surface included five routes by coupling with CO₂, i to v (**Figure 5b**). For the first route (2NH₃-CO₂) on Pd(111), the energy barrier of the reaction between NH₃ and CO₂ to form urea and H₂O, is 0.85 eV. For the second route (2NH₂-2H-CO₂) on Pd(111), the first nucleophilic addition, which happens between Pd-NH₂ and CO₂ to form carbamate, exhibits the an energy barrier of 0.49 eV. The energy barrier of the second nucleophilic addition is 0.36 eV (V'→VI'), and the rest of the steps are "down-hill". For the third throughout to fifth route (2NH-4H-CO₂ on Pd(111) (iii) and Pd step sites (v), and 2NH₂-2H-CO₂ on Pd step, iv), all the steps are "down-hill". The low-barrier free energy diagram suggests that five routes are all feasible for urea formation, with routes iii, iv and v to be the most likely ones.

In summary, this study reports the first demonstration that solar urea can be synthesized in a single step from NH₃ and CO₂ under ambient temperature and pressure conditions catalyzed by Pd/LTA-3A. The Pd/LTA-3A serves multiple functions: (a) Pd acts as a photothermal catalyst to drive the dissociation of NH₃ to surface Pd-NH₂, Pd-NH, and Pd-H intermediates, which react with CO₂ to form urea; (b) LTA-3A removes the by-product, H₂O, thereby shifting the reaction equilibrium towards urea formation, and (c) LTA-3A stabilizes the Pd nanoparticles against sintering. This synthetic strategy utilizes solar energy as the only energy source, circumventing the almost century-old energy and greenhouse-gas intensive Bosch-Meiser process. Significantly,

ammonium carbamate, the intermediate product of the two-step Bosch-Meiser process, will decompose under the ambient conditions used in this solar urea study. A one-step synthesis of the type reported has the potential to diminish the complexity of the process and equipment design for industrial production of urea. Although the current conversion and production rates need to be improved for a technologically viable process, there is much room for engineering the photocatalyst and photoreactor performance metrics. We envision the breakthrough described herein will inspire research aimed at replacing the century-old fossil-powered Bosch-Meiser urea process with an eco-friendly solar powered version, a first step towards the development of sustainable, modular plants for the distributed production of urea on farms.

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- [1] a) Expert Market Research, **2021**; b) Nutrien, **2019**; c) IHS Markit, **2016**.
- [2] a) Yara, **2018**; b) International Fertilizer Association, **2019**.
- [3] a) United Nations New York, **2017**; b) W. Stewart, T. Roberts, *Procedia Eng.* **2012**, *46*, 76-82; c) International Fertilizer Association, **2018**.
- [4] A. H. Conner, *Polymeric materials encyclopedia* **1996**, *11*, 8496-8501.
- [5] Centre for Science and Environment, **2019**.
- [6] a) X. Xiang, L. Guo, X. Wu, X. Ma, Y. Xia, *Environ. Chem. Lett.* **2012**, *10*, 295-300; b) N. Yahya, S. Qureshi, Z. ur Rehman, B. Alqasem, C. F. Kait, *J. Magn. Magn. Mater.* **2017**, *428*, 469-480.
- [7] C. Chen, X. Zhu, X. Wen, Y. Zhou, L. Zhou, H. Li, L. Tao, Q. Li, S. Du, T. Liu, *Nat. Chem.* **2020**, *12*, 717-724.
- [8] Y. Feng, H. Yang, Y. Zhang, X. Huang, L. Li, T. Cheng, Q. Shao, *Nano Lett.* **2020**, *20*, 8282-8289.

COMMUNICATION

- [9] M. Yuan, J. Chen, Y. Bai, Z. Liu, J. Zhang, T. Zhao, Q. Wang, S. Li, H. He, G. Zhang, *Angew. Chem. Int. Ed.* **2021**, 133, 11005-11013.
- [10] a) K. K. Al-Shammeri, J. M. Saleh, *J. Phys. Chem.* **1986**, 90, 2906-2910; b) J. C. Ganley, F. Thomas, E. G. Seebauer, R. I. Masel, *Catal. Lett.* **2004**, 96, 117-122; c) S. Stolbov, T. S. Rahman, *J. Chem. Phys.* **2005**, 123, 204716; d) Z. Jiang, Q. Pan, M. Li, T. Yan, T. Fang, *Appl. Surf. Sci.* **2014**, 292, 494-499.
- [11] a) Y. Xu, L. Chen, X. Wang, W. Yao, Q. Zhang, *Nanoscale* **2015**, 7, 10559-10583; b) S. Sarina, H. Y. Zhu, Q. Xiao, E. Jaatinen, J. Jia, Y. Huang, Z. Zheng, H. Wu, *Angew. Chem. Int. Ed.* **2014**, 53, 2935-2940; c) G. Fan, S. Qu, Q. Wang, C. Zhao, L. Zhang, Z. Li, *J. Appl. Phys.* **2011**, 109, 023102; d) K. Sugawa, H. Tahara, A. Yamashita, J. Otsuki, T. Sagara, T. Harumoto, S. Yanagida, *ACS Nano* **2015**, 9, 1895-1904; e) J. Jia, P. G. O'Brien, L. He, Q. Qiao, T. Fei, L. M. Reyes, T. E. Burrow, Y. Dong, K. Liao, M. Varela, S. J. Pennycook, M. Hmadeh, A. S. Helmy, N. P. Kherani, D. D. Perovic, G. A. Ozin, *Adv. Sci.* **2016**, 3, 1600189.
- [12] M. Ghodhbene, F. Bougie, P. Fongarland, M. C. Iliuta, *Can. J. Chem. Eng.* **2017**, 95, 1842-1849.
- [13] Y. Xiong, J. Chen, B. Wiley, Y. Xia, Y. Yin, Z.-Y. Li, *Nano Lett.* **2005**, 5, 1237-1242.
- [14] M. M. Yassine, E. Dabek-Zlotorzynska, V. Celo, *J. Chromatogr. A* **2012**, 1229, 208-215.
- [15] a) K. Zangger, I. M. Armitage, *J. Magn. Reson.* **1998**, 135, 70-75; b) I. Wawer, V. Koleva, *J. Mol. Struct.* **1995**, 344, 251-256.
- [16] a) X. Wang, V. Schwartz, J. C. Clark, X. Ma, S. H. Overbury, X. Xu, C. Song, *J. Phys. Chem. C* **2009**, 113, 7260-7268; b) W. C. Wilfong, C. S. Srikanth, S. S. Chuang, *ACS Appl. Mater. Interfaces* **2014**, 6, 13617-13626. c) Sayan, Ş., Kantcheva, M., Suzer, S., Uner, D. *J. Mol. Struct.* **1999**, 480, 241-245. d) Mao, C., Li, H., Gu, H., Wang, J., Zou, Y., Qi, G., Xu, J., Deng, F., Shen, W., Li, J., Liu, S., Zhao, J., Zhang, L. *Chem* **2019**, 5, 2702-2717. e) Andrews, L., Wang, X., Alikhani, M. E., Manceron, L. *J. Phys. Chem. A* **2001**, 105, 3052-3063.

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Direct urea synthesis from NH₃ and CO₂ was achieved over Pd/LTA-3A powered solely by solar energy. Pd nanoparticles serve the dual function of catalyzing the dissociation of NH₃ and providing the photothermal driving force for reaction with CO₂, while the absorption capacity of LTA-3A removes by-product H₂O, shifting the equilibrium towards urea production.