LETTER

In Situ Identification of NNH and N$_2$H$_2$ by Using Molecular-Beam Mass Spectrometry in Plasma-Assisted Catalysis for NH$_3$ Synthesis

Hao Zhao, Guohui Song, Zhe Chen, Xiaofang Yang, Chao Yan, Shota Abe, Yiguang Ju, Sankaran Sundaresan, and Bruce E. Koel*

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ABSTRACT: Ammonia synthesis at 533 K and atmospheric pressure was investigated in a coaxial dielectric barrier discharge (DBD) plasma reactor without packing and with porous γ-Al$_2$O$_3$, 5 wt % Ru/γ-Al$_2$O$_3$, or 5 wt % Co/γ-Al$_2$O$_3$ catalyst particles. Gas-phase species were monitored *in situ* using an electron impact molecular-beam mass spectrometer (EI-MBMS). Gas-phase species NNH and N$_2$H$_2$ were first identified under common conditions of plasma-assisted ammonia synthesis and were present at levels comparable to that of NH$_3$ in the plasma discharge. Concentrations of NNH, N$_2$H$_2$, and NH in a reactor packed with γ-Al$_2$O$_3$ or other particles were lower than those observed in an empty reactor, while the concentration of NH$_3$ increased. These observations point to the importance of NNH and N$_2$H$_2$ in plasma-assisted surface reactions in ammonia synthesis. Reaction pathways of direct adsorption of gas-phase NNH and N$_2$H$_2$ on solid surfaces and subsequent reactions were proposed. This study demonstrated that *in situ* identification of gas-phase species *via* EI-MBMS provides a powerful approach to study the kinetics of plasma-assisted catalysis.
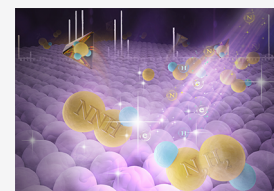
Ammonia synthesis from N$_2$ and H$_2$ gases *via* the Haber−Bosch (HB) process[1−3] is an important industrial process, producing ∼160 million tons of ammonia yearly. This process requires a high temperature (∼700 K) and a high pressure (∼100 bar), and it consumes 1−2% of the world's energy production.[4] With the increase in renewable sources of electricity and the desire to decrease the capital costs and provide distributed capabilities for NH$_3$ synthesis with rapid startup and shutdown, there has been a great interest in using nonequilibrium plasma generated by electric discharges to carry out ammonia synthesis at lower temperatures and pressures by plasma-assisted heterogeneous catalysis.[5−18] To date, plasma-assisted catalysis for NH$_3$ synthesis has a much lower energy conversion efficiency than the HB process, and significant improvements are needed for it to become a viable technology.[19,20] Such advances are limited by our incomplete understanding of the complex gas-phase chemistry in the N$_2$ + H$_2$ plasma and the interaction of the gas-phase species generated by the plasma with catalytically active surfaces, which in turn stems from the dearth of *in situ* and *operando* characterization methods that can be applied to plasma reactors.

In the present study, we have probed the composition of the gas phase in a coaxial dielectric barrier discharge (DBD) plasma-assisted catalytic reactor for ammonia synthesis by using a custom interface connected to a time-of-flight (TO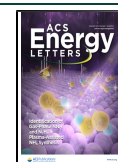F) molecular-beam mass spectrometer (MBMS) system, which is shown schematically in Figure 1. The atmospheric-pressure N$_2$−H$_2$−He DBD plasma was generated by an alternating current (AC) power source at 12 kV and a frequency of 20 kHz. The MBMS was operated to specifically record signals for N$_2$, H$_2$, NH$_3$, NH, NH$_2$, NNH, N$_2$H$_2$, and N$_2$H$_4$ with a mass resolution of ∼1000. Details of the reactor system, species calibrations, measurement uncertainty, and the catalyst preparation method are described in the Supporting Information (SI). In all of the experiments reported below, the reactor temperature was 533 K. The plasma power was estimated to be 7.1 W in the empty reactor and 8.5 W in the reactor loaded with various particles.

MBMS measurements were made while the DBD reactor was operated empty with no packing or packed with porous γ-Al$_2$O$_3$ particles or 5 wt % Ru/γ-Al$_2$O$_3$ or Co/γ-Al$_2$O$_3$ catalyst particles. The sampling nozzle was located very close to the downstream end of the reactor (see Figure 1). Figure 2 shows the NH$_3$ concentrations measured by MBMS for various cases. The corresponding NH$_3$ synthesis rates that were determined
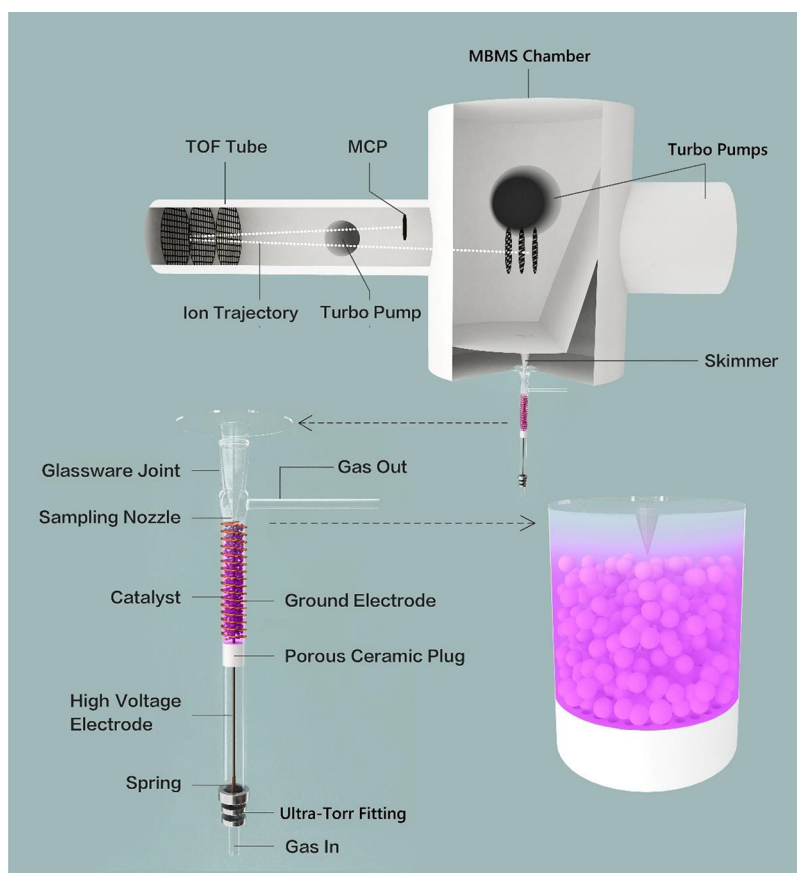
Figure 1. Schematic of the molecular-beam mass spectrometer (MBMS) and the custom interface for *in situ* sampling of gas-phase species in the plasma-assisted catalytic reactor.
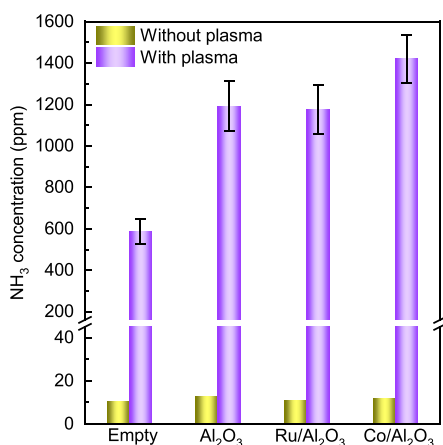

Figure 2. NH$_3$ concentrations in the gas phase detected by MBMS during DBD plasma-assisted NH$_3$ synthesis. Data were obtained for an empty reactor and for the reactor loaded with porous γ-Al$_2$O$_3$, 5 wt % Ru/γ-Al$_2$O$_3$, or 5 wt % Co/γ-Al$_2$O$_3$ particles. Reaction conditions: 1 atm, 533 K, total flow rate 353 sccm, feed gas 20% N$_2$/10% H$_2$/70% He, catalyst particle mass 1.2 g.

using the flow rate and measured NH$_3$ concentrations can be found in Figure S1. The NH$_3$ concentration was below the detection limit of ~20 ppm in this study when the plasma was off, but its concentration greatly increased when the plasma was turned on. Packing the plasma zone with γ-Al$_2$O$_3$ support beads led to a doubling of the NH$_3$ concentration from that observed in the empty tube plasma reactor. Further improve-

ment of the NH$_3$ yield by ~20% was obtained using a 5 wt % Co/γ-Al$_2$O$_3$ catalyst. In contrast, the 5 wt % Ru/γ-Al$_2$O$_3$ catalyst gave nearly the same NH$_3$ yield as the γ-Al$_2$O$_3$ support, even though Ru is a highly active catalyst for the thermal catalytic synthesis of NH$_3$. Our results are qualitatively consistent with those reported by Mehta *et al.*,[21] who found Co to be a more effective catalyst than Ru under plasma conditions.

N$_2$H$_2$ (30 amu), NNH (29 amu), and NH (15 amu) were detected and quantified in plasma-assisted NH$_3$ synthesis for the first time, as shown in Figure 3. Although NH$_2$ (16 amu) was also detected (see Figure S2), we regard its level as noise, as it sat close to our detection limit with some random positive/negative values after signal calibrations. In the absence of plasma, the NNH, N$_2$H$_2$, and NH concentrations were ~30, 5, and 5 ppm, respectively (see Figure 3). However, with the plasma on, their concentrations were at least 1 order of magnitude higher. The presence of these reactive species at such high levels suggests that plasma catalysis modeling efforts should consider their possible role in plasma-assisted NH$_3$ synthesis. Adding γ-Al$_2$O$_3$ pellets to the reactor decreased the concentrations of NNH, N$_2$H$_2$, and NH (Figure 3), while the NH$_3$ concentration increased (Figure 2). A plausible explanation for these directional changes in the concentration levels would be that gas-phase NNH, N$_2$H$_2$, and NH interact with the solid surface and participate in NH$_3$ synthesis on it.

N$_2$ scrambling experiments were performed using a 20% ^{14}N$_2$ (28 amu)/10% ^{15}N$_2$ (30 amu)/70% He gas mixture with and without plasma. The concentrations of ^{14}N^{15}N (29 amu)
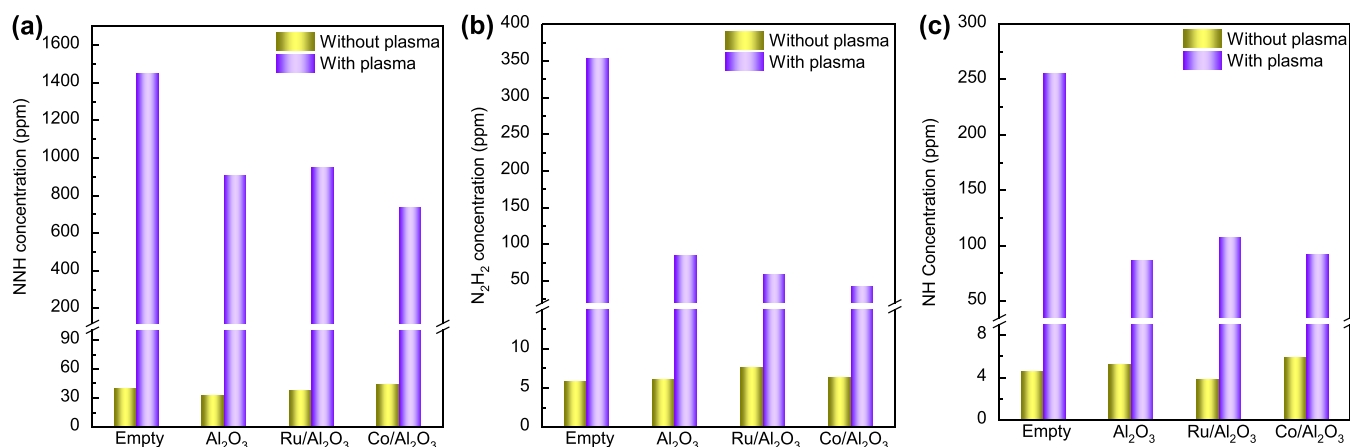
Figure 3. Concentrations of gas-phase (a) NNH, (b) N_2H_2, and (c) NH detected by MBMS during DBD plasma-assisted NH_3 synthesis. Data were obtained for an empty reactor and for the reactor loaded with porous γ-Al_2O_3, 5 wt % Ru/γ-Al_2O_3, or 5 wt % Co/γ-Al_2O_3 particles. See the Figure 2 caption for the reaction conditions.

measured using MBMS under different conditions are presented in Figure 4. The $N^{14}N^{15}$ (29 amu) concentration
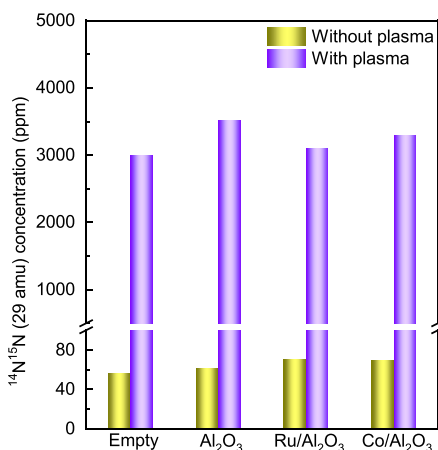

Figure 4. $^{14}N^{15}N$ (29 amu) concentrations determined by MBMS during N_2 scrambling experiments in the DBD reactor. Data were obtained for an empty reactor and for a reactor loaded with porous γ-Al_2O_3, 5 wt % Ru/γ-Al_2O_3, or 5 wt % Co/γ-Al_2O_3 particles. Reaction conditions: 1 atm, 533 K, total flow rate 353 sccm, feed gas 20% $^{14}N_2$ (28 amu)/10% $^{15}N_2$ (30 amu)/70% He, catalyst particle mass 1.2 g.

in the presence of plasma is 75−80 times higher than that observed in the absence of plasma. The difference in the $N^{14}N^{15}$ (29 amu) concentrations observed in an empty reactor and a reactor loaded with particles is small, indicating that only the solid surfaces contributed negligibly to the formation of $N^{14}N^{15}$ (29 amu) through dissociative adsorption of $^{14}N_2$ (28 amu). Such a weak contribution from the heterogeneous reactions is likely due to the large activation barriers for the associative desorption of N adatoms to produce gas-phase N_2. (Desorption of a N adatom to form gas-phase N radical is much less likely.)

It is well-established that in the HB process the dissociative adsorption of N_2 is the rate-determining step because of its large activation energy barrier.[22,23] It has been suggested that plasma assists the catalysis by generating vibrationally excited nitrogen molecules, $N_2(v)$, which can dissociatively adsorb at a higher rate than ground-state N_2 molecules.[21] Plasma also produces highly reactive radicals that can adsorb onto surfaces and also participate in Eley−Rideal reactions. In the context of ammonia synthesis, the formation of N, H, NH, NH_2, and NH_3 in the gas phase[3,24,25] and their interactions with solid surfaces[3,24,26,27] have been examined in plasma kinetic model analysis. The presence of NH_x species in the gas-phase plasma or on catalyst surfaces in plasma has been demonstrated in experiments by using optical emission spectroscopy,[28] X-ray photoelectron spectroscopy,[14] and inelastic neutron scattering.[29] Hwang and Mebel[30] calculated rate constants for thermal NH_3 synthesis in the gas phase including intermediates such as NH, NH_2, NNH, and N_2H_2; however, according to their rate models, the concentrations of these intermediates in the gas phase are very low at the temperature used in our study, and therefore, they play an insignificant role in thermal reactions. Winter et al.[31] identified surface reaction intermediates such as N_2H_y in plasma catalytic ammonia synthesis, although these species were not separately identified and quantified. To the best of our knowledge, NNH and N_2H_2 have not been considered well previously in plasma catalytic experiments and kinetic modeling, likely because there has been no direct experimental identification indicating their presence at appreciable levels. The present study provides this missing evidence. Below we *hypothesize* reaction steps that could be important in a plasma environment and should be examined more closely in future studies.

Gas-phase NNH can be formed from ground-state or excited N_2 through the following reactions:

$$N_2(g) + H(g) \rightleftarrows NNH(g) \tag{R1}$$

$$N_2(v) + H(g) \rightleftarrows NNH(g) \tag{R2}$$

The NNH(g) formed in this manner can participate in reactions such as R3 and R4 to yield N_2H_2(g):

$$NNH(g) + H(g) \rightleftarrows N_2H_2(g) \tag{R3}$$

$$NNH(g) + H_2(g) \rightleftarrows N_2H_2(g) + H(g) \tag{R4}$$
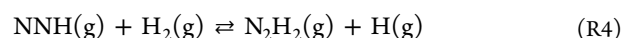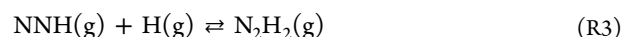
Ground-state or excited NNH(g) and N_2H_2(g) may also participate in elementary reaction steps involving sites on solid surfaces:

$$NNH(g) + s \rightleftarrows NNH(s) \tag{R5}$$

$$NNH(g) + H(s) \rightleftarrows N_2H_2(s) \tag{R6}$$

$$NNH(s) + s \rightleftarrows N(s) + NH(s) \tag{R7}$$

$$N_2H_2(g) + s \rightleftarrows N_2H_2(s) \tag{R8}$$

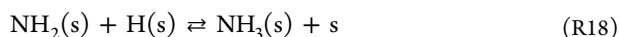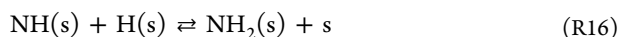$$N_2H_2(s) + s \rightleftarrows 2NH(s) \tag{R9}$$
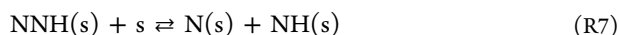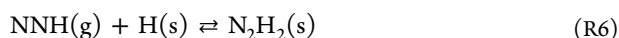
In addition, N(s), NH(s), and H(s) can form *via* direct adsorption of N(g), NH(g), and H(g), which have been considered in plasma kinetic model analysis already.[3]

$$N(g) + s \rightleftarrows N(s) \tag{R10}$$

$$H(g) + s \rightleftarrows H(s) \tag{R11}$$

$$NH(g) + s \rightleftarrows NH(s) \tag{R12}$$

The surface intermediates N(s) and NH(s) can react further with H(g) and H(s) through Eley–Rideal and Langmuir–Hinshelwood steps to produce $NH_2(s)$ and then $NH_3(s)$, which have also been included in plasma kinetic analysis previously.[3]

$$N(s) + H(g) \rightleftarrows NH(s) \tag{R13}$$

$$N(s) + H(s) \rightleftarrows NH(s) + s \tag{R14}$$

$$NH(s) + H(g) \rightleftarrows NH_2(s) \tag{R15}$$

$$NH(s) + H(s) \rightleftarrows NH_2(s) + s \tag{R16}$$

$$NH_2(s) + H(g) \rightleftarrows NH_3(s) \tag{R17}$$

$$NH_2(s) + H(s) \rightleftarrows NH_3(s) + s \tag{R18}$$

One can enumerate additional possible elementary reaction steps in the gas phase involving NNH(g) and $N_2H_2(g)$, but we do not present them here because the principal purpose of the above discussion is to point to the need for further study of reaction steps involving NNH(g) and $N_2H_2(g)$. On the basis of bond order considerations, reactions R7 and R9 can be expected to involve much smaller activation barriers than $N_2(s) + s \rightleftarrows 2N(s)$.

Our experimental results support the above reaction steps qualitatively. A large amount of NNH(g) is formed even in a plasma reactor with no packing (see Figure 3a), supporting the notion that NNH(g) is formed in the gas phase (through reactions such as R1 and R2). It is clear from Figure 3b that $N_2H_2(g)$ is present at a much lower level than NNH(g), which is consistent with slow conversion of NNH(g) to $N_2H_2(g)$ (through reactions such as R3 and R4). We did not detect any $NH_2(g)$, which implies either that it is not formed in appreciable amounts in the gas phase or that it is converted to other species very rapidly.

The ammonia concentration in a plasma reactor loaded with solid particles is higher than that afforded by an empty plasma reactor (see Figure 2). Furthermore, the concentrations of NNH(g) and $N_2H_2(g)$ were smaller in the presence of packing (see Figure 3). Remarkably, the magnitude of the difference in the NNH(g) levels observed in the empty reactor and the reactor loaded with γ-Al_2O_3 particles (see Figure 3a) is comparable to the difference in the $NH_3(g)$ concentrations (see Figure 2), strongly suggesting that the presence of the solid surfaces facilitates the conversion of NNH to NH_3, which can occur *via* a combination of direct adsorption, Langmuir–

Hinshelwood, and Eley–Rideal reaction steps (such as steps R5 to R18).

It should be noted that the concentration of $NH_3(g)$ obtained with 5 wt % Co/γ-Al_2O_3 is greater than that obtained with γ-Al_2O_3, while the NNH(g) concentrations manifest the opposite trend (almost quantitatively). Thus, it could simply be that 5 wt % Co/γ-Al_2O_3 is more effective than γ-Al_2O_3 in converting NNH to NH_3.

The results of the N_2 scrambling experiments (Figure 4) do not provide direct support for the importance of dissociative adsorption of $N_2(v)$ in ammonia synthesis; strictly speaking, they do not refute that hypothesis either.

In summary, the gas-phase species N_2H_2, NNH, and NH have been identified using *in situ* molecular-beam mass spectrometry for the first time in a DBD plasma reactor operating at 533 K and atmospheric pressure. Experiments were performed in the plasma reactor without any packing or with porous γ-Al_2O_3 particles or 5 wt % Ru/γ-Al_2O_3 or Co/γ-Al_2O_3 catalyst particles. The gas-phase species NNH and N_2H_2 were first identified under common conditions of plasma-assisted ammonia synthesis. The presence of γ-Al_2O_3 particles in the reactor leads to a significant increase in the rate of ammonia synthesis, which is accompanied by a decrease in the levels of NNH, N_2H_2, and NH in the gas phase. These observations support the importance of NNH and N_2H_2 interactions for NH_3 production in a plasma reactor. The use of Ru/γ-Al_2O_3 catalysts does not cause higher ammonia synthesis rates, but the use of Co/γ-Al_2O_3 catalysts does. We propose that direct adsorption of gas-phase NNH and N_2H_2 on solid surfaces and a combination of Eley–Rideal and Langmuir–Hinshelwood reactions of adsorbed NNH and N_2H_2 are important in plasma-assisted reactions on solid surfaces. The present study also shows that MBMS is a powerful technique for *in situ* identification of gas-phase molecules and radicals in plasma-assisted reactions even at atmospheric pressure, where the lifetimes of reactive species are relatively short.

■ ASSOCIATED CONTENT

⑤ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsenergylett.1c02207.

> Details of the experimental procedures; details of the MBMS system; concentration calibrations for stable molecules and radicals; fragmentation signal corrections in MBMS; details of catalyst preparation; plot of the net synthesis rate of NH_3 for the sampled gas from the reactor; plot of concentration of NH_2 for the sampled gas from the reactor (PDF)

■ AUTHOR INFORMATION

Corresponding Author

Bruce E. Koel − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States;* ⦿ orcid.org/0000-0002-0032-4991; Email: bkoel@princeton.edu

Authors

Hao Zhao − *Department of Chemical and Biological Engineering and Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, United States;* Present Address: College of

Engineering, Peking University, Beijing 100871, China;
Email: h.zhao@pku.edu.cn; ● orcid.org/0000-0002-8879-9595

Guohui Song − *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, United States; School of Energy and Power Engineering, Nanjing Institute of Technology, Nanjing 211167, China;* ● orcid.org/0000-0002-2749-427X

Zhe Chen − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States*

Xiaofang Yang − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States; Princeton Nuenergy Inc., Princeton, New Jersey 08540, United States*

Chao Yan − *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, United States;* ● orcid.org/0000-0002-2415-6080

Shota Abe − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States*

Yiguang Ju − *Department of Mechanical and Aerospace Engineering, Princeton University, Princeton, New Jersey 08544, United States*

Sankaran Sundaresan − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08544, United States;* ● orcid.org/0000-0002-5868-1975

Complete contact information is available at:
https://pubs.acs.org/10.1021/acsenergylett.1c02207

Notes
The authors declare no competing financial interest.

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