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SUSTAINABLE NITROGEN FIXATION BY PULSED AIR DISCHARGE*

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Considering the increasing demand for fertilizers to support the global food supply, as well as the high-energy consumption and environmental concerns caused by industrial nitrogen fixation (i.e., Haber–Bosch process), there is a critical need to develop and integrate more sustainable, green-chemistry-based processes of nitrogen fixation. Energy-efficient and environmentally benign alternatives for NH_3 synthesis are urgently needed, especially the green-chemistry, light- or electricity-driven processes (*i.e.*, photo-catalysis, electro-catalysis, and non-thermal plasma (NTP)) using renewable energy (*i.e.*, solar and wind), to near the ultimate goal of zero carbon emissions [1].

As an electrically driven process, NTPs have been extensively investigated as an alternative for decentralized NO_x or ammonia production powered by renewable clean energy sources [2]. Emerging NTP-enabled nitrogen fixation processes are used to convert N_2/H_2 or N_2/H_2O directly to NH_3. On the other hand, the indirect approach involving plasma nitrogen oxidation ($N_2 \rightarrow NO_x$) and further catalytic reduction to ammonia ($NO_x \rightarrow NH_3$) have been proposed with the obtained energy efficiency of 4.6 MJ mol^{-1} NH_3, which is more than four times lower than the state-of-the-art plasma-enabled NH_3 synthesis from N_2 and H_2 with reasonable yields (>1 %) [3]. However, the issue of decoupling the challenges of molecular activation and product selectivity remains.

Recently, this work reveals the underlying reaction mechanisms for sustainable nitrogen fixation in nanosecond repetitive plasmas in spark discharges in the air by the combinatorial experiment, process diagnostics, and modeling investigations [4]. It is revealed that more than 50% of the generated NO originate from the chain reactions of O and N radicals with vibrationally excited N_2 and O_2 molecules ($O + N_2(\upsilon) \rightarrow NO + N$ and $N + O_2(\upsilon) \rightarrow NO + O$). Most NO_2 molecules are formed by further oxidation of NO species ($NO + O \rightarrow NO_2$). The presence of O and N spectral lines at the post-discharge stage further confirmed the important role of free-radical-chain reactions. These results provide new insights into sustainable and decentralized NO_x production.

It should be pointed out that the current energy cost of the plasma-based NO_x synthesis process is however still too high to be competitive with the electrolysis-based Haber–Bosch process combined with the Ostwald process, which will limit its large-scale industrialization [5]. Alternatively, we are now working on directly synthesizing compound fertilizer (*i.e.*, NO_x^- and trace metal ions) by pulsed air discharge to avoid the NH_3 synthesis pathways and testing their effects on pea seed's germination speed [6].

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