Photoelectrochemical Nitrogen Fixation for Ammonia Synthesis Using Hybrid Plasmonic Nanostructures

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ECS Meeting Abstracts, Volume MA2020-02, L04: Photocatalysts, Photoelectrochemical Cells, and Solar Fuels 11**Citation** Mohammadreza Nazemi and Mostafa El-Sayed 2020 *Meet. Abstr.* **MA2020-02** 3101

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DOI

https://doi.org/10.1149/MA2020-02613101mtgabs

Abstract

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Cost-effective production of ammonia via (photo)electrochemical nitrogen reduction reaction (NRR) hinges on N_2 electrolysis at high current densities with suitable selectivity and activity [1, 2]. In this talk, we report our findings in electrochemical NRR for ammonia synthesis using porous bimetallic Pd-Ag nanocatalysts in both gas-phase and liquid-phase electrochemical cells at current densities above 1 mA cm^{-2} under ambient conditions. While the gas-phase cell has lower Ohmic losses and higher energy efficiency, the liquid-phase cell achieved higher selectivity and Faradaic efficiency, attributed to the presence of concentrated N_2 molecules dissolved in an aqueous electrolyte and the hydration effects. The liquid cell demonstrated notable performance for electrocatalytic NRR, achieving an NH_3 production rate of 45.6 μg cm^{-2} h^{-1} at a cathodic potential of -0.6 V (vs. RHE) and current density of 1.1 mA cm^{-2}, corresponding to a Faradaic efficiency of ~19.6% and an energy efficiency of ~9.9%. Similarly, the gas-phase cell achieved an NH_3 yield rate of 19.4 μg cm^{-2} h^{-1} at -0.07 V (vs. RHE) and 1.15 mA cm^{-2} with a Faradaic efficiency of 7.9% and an energy efficiency of 27.1%. In addition, the photoelectrocatalytic activities of these hybrid plasmonic nanostructures under illumination and dark conditions will be explored and photocurrent and photovoltage responses will be reported. *Operando* surface-enhanced Raman spectroscopy (SERS) is

used to identify the intermediate species relevant to NRR at the solid-liquid (electrode-electrolyte) interface. This work highlights the importance of design and optimization of cell configuration in addition to the modification of the catalyst to achieve high-performance N_2 electrolysis for ammonia synthesis. It also demonstrates the use of *operando* SERS as a powerful technique for unraveling reaction mechanisms for (photo)electrocatalytic phenomenon.

[1] M. Nazemi, L. Soule, M. Liu, M. A. El-Sayed, "Ambient Ammonia Electrosynthesis from Nitrogen and Water by Incorporating Palladium in Bimetallic Gold-Silver Nanocages" *Journal of The Electrochemical Society*, 167(5), p. 054511, 2020.

[2] M. Nazemi, M. A. El-Sayed, "Plasmon-Enhanced Photo(electro)chemical Nitrogen Fixation under Ambient Conditions Using Visible Light Responsive Hybrid Hollow Au−Ag_2O Nanocages" *Nano Energy*, vol. 63, 103886, 2019.