Synergistic Cyanamide Functionalisation and Charge-Induced Activation of Nickel/Carbon Nitride for Enhanced Selective Photoreforming of Ethanol

Denny Gunawan, Cui Ying Toe, Priyank Kumar, Jason Scott, and Rose Amal**

Particles and Catalysis Research Group, School of Chemical Engineering, The University of New South Wales (UNSW), Sydney, NSW 2052, Australia
First author: denny.gunawan@unsw.edu.au
**Corresponding authors: c.toe@unsw.edu.au, r.amal@unsw.edu.au*

Photoreforming is a promising alternative to water splitting for H_2 generation due to the favourable organic oxidation half-reaction and the potential to simultaneously produce solar fuel and value-added chemicals.[1-3] Recently, carbon nitride has received significant attention as an inexpensive photocatalyst for the photoreforming process.[4, 5] However, the application of carbon nitride continues to be hampered by its poor photocatalytic performance. Herein, we report for the first time a synergistic modification of *in situ* photodeposited Ni cocatalyst on carbon nitride *via* cyanamide functionalisation and solid/liquid interfacial charge-induced activation by using excess Ni^{2+} ions. Synergism between the cyanamide functionalisation and charge-induced activation by the excess Ni^{2+} ions invokes enhanced activity, selectivity, and stability during ethanol photoreforming. A H_2 evolution rate of 2.32 mmol h^{-1} g^{-1} in conjunction with an acetaldehyde production rate of 2.54 mmol h^{-1} g^{-1} were attained for the Ni/NCN-CN. The H_2 evolution rate and elevated acetaldehyde selectivity (above 98%) remained consistent under prolonged light illumination. To understand the origin of the complementary promotional effects, the contributions of cyanamide groups and excess Ni^{2+} ions to selective ethanol photoreforming are decoupled and systematically investigated. The cyanamide functionality on carbon nitride was found to promote ethanol oxidation reaction *via* hole consumption, meanwhile enabling effective electron transfer to the Ni cocatalyst for H_2 evolution. Concomitantly, excess Ni^{2+} ions remaining in solution created a positively-charged environment on the photocatalyst surface which improved charge carrier utilisation and ethanol adsorption. The work highlights both the importance of carbon nitride functionality and charge on the photocatalyst surface in developing a selective photocatalytic reforming system.

References

1. Toe, C. Y., Tsounis, C., Zhang, J., Masood, H., Gunawan, D., Scott, J., Amal, R. *Energy Environ. Sci.* **2021**, *14* (3), 1140-1175.
2. Uekert, T., Pichler, C. M., Schubert, T., Reisner, E. *Nat. Sustain.* **2020**, *4*, 383-391.
3. Ramis, G., Bahadori, E., Rossetti, I. *Int. J. Hydrog. Energy* **2021**, *46* (22), 12105-12116.
4. Kasap, H., Caputo, C. A., Martindale, B. C., Godin, R., Lau, V. W., Lotsch, B. V., Durrant, J. R., Reisner, E. *J. Am. Chem. Soc.* **2016**, *138* (29), 9183-9192.
5. Uekert, T., Kasap, H., Reisner, E. *J. Am. Chem. Soc.* **2019**, *141* (38), 15201-15210.