Oral Presentation-32

Supramolecular-Assisted Eutectic Synthesis of Nickel-Incorporated Carbon Nitride Frameworks for Photon-Assisted Catalytic CO2 Reduction

Hariprasad Narayanan[1,2]*, Harindranthan Nair[2], and Balasubramanian Viswanathan[1]*

1National Centre for Catalysis Research, Department of Chemistry, Indian Insititute of Technology Madras, Chennai-600036, Tamil Nadu, India

2School of Environmental Studies, Cochin University of Science and Technology, Cochin-682022, Kerala, India. Email: hariprasadmandur@gmail.com; bviswanathan@gmail.com

ABSTRACT

This study presents a novel supramolecular-assisted eutectic synthesis approach for developing carbon nitride (CN) materials tailored for photon-assisted CO2 reduction. Melamine cyanurate was used as a precursor with nickel incorporation through NiCl2-CsCl and NiCl2-KCl eutectic salt mixtures to synthesize Ni-incorporated CN frameworks (gCN-NiCs and gCN-NiK). The materials were characterized using XRD, XPS, nitrogen adsorption-desorption, and UV-vis spectroscopy. Results revealed significant structural modifications upon Ni incorporation, including alterations in surface area, pore characteristics, and electronic properties. Photon-assisted CO2 reduction experiments demonstrated superior performance of Ni-incorporated materials compared to bulk g-CN, with gCN- NiCs exhibiting the highest yield for methane and methanol production. Detailed mechanistic insights into the CO2 reduction process were proposed, considering both direct and indirect pathways. Band structures constructed using valence band XPS and diffuse reflectance spectroscopy data provided crucial understanding of charge transfer processes. The gCN-NiCs catalyst showed optimal band edge positions, higher C values, NSC% and greater DP/SA ratios, explaining its superior catalytic activity. This work introduces a novel synthesis approach for tailoring CN materials and offers valuable insights into designing efficient photon-assisted CO2 reduction catalysts. The findings underscore the potential of supramolecular-assisted eutectic synthesis in developing advanced materials for solar fuel production, contributing significantly to sustainable energy conversion technologies.

Note: DP/SA and NSC% are new proposed metrics introduced in the work to assess the incident photon- structure-property-performance relationships which are respectively called D-parameter/surface area and normalised surface concentration of the surface functionalities.

Keywords: carbon nitride, supramolecular synthesis, photocatalysis, CO2 reduction, band structure

References

1. Barrio, J.; Shalom, M. Rational Design of Carbon Nitride Materials by Supramolecular Preorganization of Monomers. ChemCatChem, 2018. 10, p. 5573–5586.

2. Zhou, Y.; Martín, A. J.; Dattila, F.; Xi, S.; Lopez, N.; Perez-Ramirez, J.; Yeo, B. S. Long-chain hydrocarbons by CO2 electroreduction using polarized nickel catalysts. Nature Catalysis, 2022. 5, p. 545–554.