Surface Plasmon-Enhanced Photo-Driven CO_2 Hydrogenation by Hydroxy Terminated Nickel Nitride Nanosheets

Saideep Singh, Rishi Verma and Vivek Polshettiwar

Department of Chemical Sciences, Tata Institute of Fundamental Research

saideep@tifr.res.in, vivekpol@tifr.res.in

Abstract:

The plasmonic photocatalytic conversion of CO_2 into valuable solar fuels and chemicals is an appealing way to recycle carbon. However, almost all visible light-active plasmonic catalysts are limited to Au, Ag, Cu, and Al, which have considerations in terms of costs, accessibility, and instability.[1] In continuation of our previous study, we demonstrate hydroxy-terminated nickel nitride (Ni_3N) nanosheets, as an alternative to these metals, as a plasmonic catalyst for CO_2 hydrogenation. The Ni_3N nanosheets showed an excellent CO production rate (ca. 1212 mmol g^{-1} h^{-1}) and 99 % selectivity towards CO under flow conditions using visible light. Photocatalytic reaction rates on excited plasmonic Ni_3N nanosheets showed super-linear power law (n) dependence on light intensity (I), with n of 6.3, which is significantly higher than conventional plasmonic metal nanoparticles. Photocatalytic quantum efficiencies on Ni_3N nanosheets increased with an increase in light intensity and reaction temperature.[2] In the presence of an electron acceptor – which would provide an alternative harvester for the hot electrons, a reduction in the CO production rate was observed, thus corroborating a hot-electron mediated mechanism.[3] The critical proof of the non-thermal effect also came from the Ni_3N nanosheets thermal stability behavior. Ni_3N nanosheets (which were thermally stable only up to 325 ^{o}C) showed stable catalytic activity for a long time (25 h), indicating that surface temperature must be below 325 ^{o}C during the plasmonic catalysis. Below this temperature, it showed poor catalytic activity in the dark. The in-situ DRIFTS study provided molecular insights into CO_2 hydrogenation and showed that the reaction proceeds via the direct dissociation pathway. The excellent photocatalytic performance of these Ni_3N nanosheets (without co-catalysts or sacrificial agents) is suggestive of the use of metal nitrides instead of conventional metal nanoparticles in the next generation of plasmonic photocatalysts.

References:

1. Camargo, C. H. P., Cortés, E. Plasmonic catalysis: From fundamentals to applications. ISBN: 978-3-527-34750-6 Wiley-VCH, Weinheim (2021).
2. Christopher, P., Xin, H., Marimuthu, A., Linic, S., Singular characteristics and unique chemical bond activation mechanisms of photocatalytic reactions on plasmonic nanostructures. *Nature Mater* **11**, 1044–1050 (2012).
3. Mascaretti, L., Naldonia, A. Hot electron and thermal effects in plasmonic photocatalysis, *J. Appl. Phys.* **128**, 041101 (2020).