Abstract

Anthropogenic CO_2 emissions from fossil fuel consumption have opened a pandora's box of climatic and sustainability problems. Reducing CO_2 into fuels and carbon-based compounds on expenditure of intermittent renewable electricity resources (solar, wind) is a promising way to store this energy and close the carbon cycle. Electrochemical CO_2 reduction (ECR) requires highly efficient, robust and selective catalysts to selectively and efficiently convert CO_2 at lower overpotentials into fuels for commercialisation. This thesis begins with studying the role of various physico-chemical properties like morphology, phase, carbonaceous support, synergism between metal and GO support, and electrode fabrication of a copper nanocatalyst in ECR activity, selectivity and stability in acetonitrile electrolyte system into CO. Similar studies were done on Cu/Cu_xO-GO catalysts in aqueous $KHCO_3$ electrolyte solutions to transform CO_2 selectively into ethylene. An interplay between the electrode/electrolyte influences the mechanism of the ECR, resulting in different products. This was found true in the case of Cu/Cu_xO-GO catalysts also, where ECR in aprotic solvent like acetonitrile yielded CO and availability of reducible protons shifted reaction selectivity towards ethylene.

High electroactive surface area accelerates the ECR activity and kinks, and porous nature causes an increase in local pH around these shapes, which impedes hydrogen evolution reaction (HER). An extensively branched dendritic morphology has these optimum properties. We studied the role of applied potential, ascorbic acid concentration, temperature and time on the morphology of resultant catalyst and optimised the dendritic structure for maximum surface area and secondary branching. A plausible mechanism for the dendritic growth in electrodeposition was also explained. In wet-dimethylsulphoxide (DMSO), the optimised structure produced 33% ethane from CO_2 at -1.5 V (NHE). HER was inhibited on these structures. A shift from production of ethane in wet-DMSO to ethylene (faradaic efficiency of 43%), in $KHCO_3$ was observed which may be due to solvent effects at the interface. Presence

of solvent at inner Helmholtz layer can alter the product profile by controlling the reducible protons available to the electrode surface. Therefore, even if the catalyst structure is same change of solvents can alter the course. The effect of solvent was found more prominent in dendritic or uneven shapes than in simple and spherical shapes.

For methane production (100) facets on smaller rhombohedral copper catalysts are very efficient for ECR. Controlling the surface texture, finesse, and homogeneity by reverse pulse currents, and presence of surface modifying ionic liquids, catalysts converting CO_2 to CH_4 with an efficiency of 67.4% and at partial current density of 38 mA/cm^2 were prepared. A study of pulse nature and additive presence was done to gain more insights about the catalyst preparation and its activity.

Catalysts having porous and high surface area increase ECR activity, an ability to adsorb CO_2 and simultaneously having an active redox system for electron transfer to CO_2 should lead to higher currents for CO_2 reduction reaction. Copper metal-organic frameworks (CuMOFs) can act both as CO_2 adsorbents as well as redox metal centres for CO_2 reduction, but their electrochemical instability limits their potential use. To surmount this problem, simple groups like NH_2 were used as replacements on free surface -COOH groups on CuMOFs. This simple transformation increased both ECR activity and electrochemical stability of these CuMOFs. HER is suppressed while hydrocarbons were favoured over simple CO.

Overall, this thesis is outlining the implementation of theoretically predicted and empirically realised catalyst properties in a single catalyst system to enhance the ECR activity and selectivity into energy-dense hydrocarbons like ethylene and methane.

Journal Publications

1. Rashid, N.; Bhat, M.A.; Ingole, P. P. Dendritic copper microstructured electrodeposits for efficient and selective electrochemical reduction of carbon dioxide into C1 and C2 hydrocarbons. Journal of CO_2 Utilization, 2020, 38, 385-397.

2. Rashid, N.; Bhat, M.A.; Goutam, U. K.; Ingole, P. P. Electrochemical reduction of CO_2 to ethylene on Cu/Cu_xO-GO composites in aqueous solution. RSC Advances, 2020, 10 (30), 17572-17581.

3. Rashid, N.; Bhat, M.A.; Das, A.; Ingole, P. P. Unprecedented Lower Over-potential for CO_2 Electro-reduction on Copper oxide Anchored to Graphene Oxide Microstructures. Journal of CO_2 Utilization, 2020, 39, 101178.

4. Nabi, S.; Sofi, F. A.; Rashid, N.; Ingole, P. P.; Bhat, M. A. Au-nanoparticle Loaded Nickel-Copper Bimetallic MOF: An Excellent Catalyst for Chemical Degradation of Rhodamine B. Inorganic Chemistry Communications, 2020, 107949.

5. Bhat, S. A.; Rashid, N.; Rather, M. A.; Pandit, S. A.; Ingole, P. P.; Bhat, M. A. Vitamin B12 functionalized N-Doped graphene: A promising electro-catalyst for hydrogen evolution and electro-oxidative sensing of H_2O_2. Electrochimica Acta, 2020, 337, 135730.

6. Butt, F. A.; Bhat, P. A.; Bhat, S. A.; Rashid, N.; Rather, M. A.; Pandit, S. A.; Ingole, P. P.; Rather, G. M.; Bhat, M. A. Transforming Micelles into Mixed Micelles: A Promising Approach to Tune the Catalytic Performance of Imidazolium Based Surface Active Ionic Liquids Toward Degradation of Rhodamine B. Physical Chemistry Chemical Physics, 2020.

7. Bhat, S. A.; Rashid, N.; Rather, M. A.; Rather, G. M.; Pandit, S. A.; Ingole, P. P.; Bhat, M. A. PdAg bimetallic nanoalloy-decorated graphene: a nanohybrid with unprecedented electrocatalytic, catalytic, and sensing activities. ACS applied materials & interfaces, 2018, 10 (19), 16376-16389.

8. Bhat, S. A.; Rashid, N.; Rather, M. A.; Rather, G. M.; Pandit, S. A.; Ingole, P. P.; Bhat, M. A. Self-assembled AuNPs on sulphur-doped graphene: a dual and highly efficient electrochemical sensor for nitrite (NO_2^-) and nitric oxide (NO). New Journal of Chemistry, 2017, 41 (16), 8347-8358.

9. Gahlawat, S.; Rashid, N.; Ingole, P. P. n-Type $Cu_2O/\alpha\text{-}Fe_2O_3$ Heterojunctions by Electrochemical Deposition: Tuning of Cu_2O Thickness for Maximum Photoelectrochemical Performance. Zeitschrift für Physikalische Chemie, 2018, 232 (9-11), 1551-1566.

10. Devnani, H.; Rashid, N.; Ingole, P. P. Copper/Cuprous Oxide Nanoparticles Decorated Reduced Graphene Oxide Sheets Based Platform for Bio- Electrochemical Sensing of Dopamine. ChemistrySelect, 2019, 4(2), 633-643.

11. Bhat, S. A.; Rashid, N.; Rather, M. A.; Pandit, S. A.; Ingole, P. P.; Bhat, M. A. Highly efficient catalytic reductive degradation of Rhodamine-B over Palladium-reduced graphene oxide nanocomposite. Chemical Physics letters, 2020, 754, 137724.

12. Yadav, S.; Singh, A.; Rashid, N.; Ghotia, M.; Roy, T. K.; Ingole, P. P.; Ray, S.; Mobin, S. M.; Dash, C.; Phosphine- Free Bis (Pyrrolyl) pyridine Based NNN- Pincer Palladium (II)

Complexes as Efficient Catalysts for Suzuki- Miyaura Cross- Coupling Reactions of Aryl Bromides in Aqueous Medium. ChemistrySelect, 2019, 3 (32), 9469-9475.

13. Rashid, N.; Bhat, M.A.; Ingole, P. P. Highly Selective Electrochemical Conversion of CO2 into Ethylene and Other C1, C2 Hydrocarbons on Micro-structured Dendritic Copper in Aqueous Solutions. (manuscript under review).

Book Chapter

Rashid, N.; Ingole, P. P. Electrochemical Reduction of CO_2 on Ionic Liquid Stabilized Reverse Pulse Electrodeposited Copper Oxides, Proceedings of the 7th International Conference on Advances in Energy Research. 10.1007/978-981-15-5955-6_147.

Papers Presented in Conferences

1. Rashid, N.; Ingole, P. P.; Dendritic semi fractal structures of copper nano-catalysts for efficient electro-reduction of CO_2 into potent fuel products (OP). International conference on Nanotechnology for better living, NIT Srinagar and IIT Kanpur, Srinagar 25-29 May, 2016.

2. Rashid, N.; Ingole, P. P.; Efficient electro reduction of CO_2 on Cu_2O/GO composites (PP). Chemical Royal Society of India national symposium in chemistry, Punjab University, Punjab 5-7 February, 2016.

3. Rashid, N.; Ingole, P. P.; Reduction of CO_2 into value added chemicals (OP). International conference for nanotechnology and material sciences, Department of Chemistry, Delhi University, New Delhi, 3-5 March, 2016.

4. Rashid, N.; Ingole, P. P.; Reduction of CO_2 on less explored semi-fractal copper structures (PP). Nano India, IIT Delhi, New Delhi, March 2017.

5. Rashid, N.; Ingole, P. P.; Electrochemical Reduction of CO_2 on Ionic Liquid Stabilized Reverse Pulse Electrodeposited Copper Oxides. (OP) ICAER Mumbai, IIT Mumbai, India 10-Dec to 12- Dec 2019.

6. Rashid, N.; Ingole, P. P.; Reverse Pulse Electrodeposition of Copper: Electrochemical reduction of CO_2 on these surfaces (OP). ECS fall meeting. Cancun Mexico 2018.

7. Rashid, N.; Ingole, P. P.; Electrochemical reduction of CO_2 on copper octahedrons. ICAEM, IISc Bangalore, India 2018.

8. Rashid, N.; Ingole, P. P.; Electrochemical Reduction of Carbon Dioxide on Copper MOFs: Effect of Ligand Functional Groups on Efficiency and Selectivity. (OP), MRS Boston, USA 01-Dec to 06 Dec 2019.

9. Rashid, N.; Ingole, P. P.; Electrochemical Reduction of CO_2 on CuMOFs. (PP) Chemical Frontiers Goa, Goa India, 20-August to 24 August, 2019.

Workshops Attended

1. Attended workshop on spectro-electrochemistry at Department of Chemistry, University of Delhi, from 17-18 June, 2015.
2. Attended "ACS on campus workshop" at IIT Delhi from 30 Oct to 1st Nov 2015.
3. Attended 'Indo-US workshop on Electrochemical Technologies, Department of Chemical engineering IIT Delhi on 2nd March, 2017.