Design and Engineering of Carbon Fixing Material Systems

by

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Through interaction with ambient light, water, oxygen, and physical stress, materials such as coatings, adhesives, and structural composite degrade. Materials fail commonly through the generation and propagation of micro-cracks, with only a miniscule amount of mass degradation often necessitating complete replacement. This degradation leads to a cycle of material production, use, and replacement fed by resource extraction and leading to waste generation. In the United States, for every ton of plastic produced we landfill over three-quarters of that amount each year. This is compared to natural systems such as plants which continuous grow, repair, and self-reinforce using carbon dioxide (CO_2) and ambient light as mass and energy sources respectively. In this thesis, we seek to study and develop mechanisms of growth and self-repair similar to living plant systems to create what we deem artificial *carbon fixing materials*, which incorporate these characteristics under non-biological conditions.

We present both experiment and computation to explore the conversion of atmospheric greenhouse gases such as carbon dioxide and methane into monomeric chemicals such as formaldehyde. A mathematical analysis of CO_2 photoreduction revealed that carbon conversion and material growth rates which rival that of living plants can be obtained with currently employed photocatalytic materials under ambient conditions. This analysis revealed that the rate limiting step in the production of carboning fixing materials acting on CO_2 is the catalytic conversion of this gas. Further, a high-throughput photocatalytic setup was constructed to analyze 12 common but unique semiconducting nanoparticle photocatalysts based on titanium dioxide, silicon carbide, and tin oxide. Overall, a universal kinetic mechanism was uncovered which accurately characterized the relationship between CO_2 conversion and production selectivity across all photocatalysts.

Methane was also investigated as an ambient carbon source for carbon fixing materials, where the rate and efficiency of this gas' oxidation with hydrogen peroxide was optimized over transition-metal modified zeolite catalysts. We revealed that iron- and copper-containing catalysts, which are reported as the most active and efficient under industrial conditions—over 30 MPa of methane partial pressure and up to 90 °C—perform poorly at ambient temperature and under one atmosphere of methane due to rapid hydrogen peroxide consumption. Instead, solely iron-containing materials showed the both the highest rate and efficiency of methane oxidation under the ambient conditions explored. To the best of our knowledge, the highest selectivity to formaldehyde to date for both carbon dioxide photoreduction and methane oxidation under the ambient conditions of room temperature and atmospheric pressure. During methane oxidation, intermediate formaldehyde was captured *in-situ* through reaction with urea to produce a urea-formaldehyde polymer. To enhance the efficiency of the reaction system, methane oxidation over the iron-modified zeolite catalyst was coupled with hydrogen peroxide generation with the enzyme *alcohol oxidase*. Finally, modeling was performed to understand carbon nanotube-based sensors and chemically-responsive materials, which may find use in the

detection and quantification of greenhouse gas emission streams and the abatement of such chemical release to the environment.

Both experimental and computation work performed in this thesis expands our understanding of the limitations and potential of imbued carbon fixation to augment the lifetime and performance characteristics of material systems. Last, this work informs the creation of future low-cost and low-carbon emission materials which we believe can reduce the environmental impact of material production as well as remediate greenhouse gas emission streams.

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