

Research Statement - Pradeep Indrakanti

CO₂ utilization refers to the generation of value-added chemicals from CO₂, thereby directly or indirectly mitigating greenhouse gas emissions. One of the technologies for CO₂ utilization involves the catalytic activation of CO₂ in the presence of light and a suitable photosensitizer to produce renewable carbon feedstocks. Solar photocatalytic reduction to produce fuels using water as the hydrogen source has the potential not only to be a means to store intermittent solar energy but also to recycle CO₂ while decreasing the use of fossil fuels. State-of-the-art CO₂ photoreduction catalysts do not perform as efficiently as the state-of-the-art catalysts in other fields of solar photochemical energy conversion (ex: H₂ photogeneration). Therefore, if the direct photoconversion of CO₂ to hydrogenated C1 products (ex: CH₃OH etc.) is to compete with other renewable energy technologies, a better understanding of the initial steps of the photoreduction of CO₂ and the development of novel catalysts with better product yields and selectivities is needed.

My graduate research has both computational and experimental components, addressing the above two issues.

Computational studies of CO₂ photoreduction on anatase TiO₂

To design efficient CO₂ photoreduction catalysts, we need to understand the intermediates and energetics of various reactions involved in the photoreduction of CO₂ in greater detail. As a first step in this process, the ground states of CO₂ chemisorbed on small clusters from various anatase surface planes were modeled. Density functional theory (DFT) calculations of CO₂ adsorbed on small TiO₂ clusters (Ti₂O₉H₁₀) extracted from the experimental (010), (001) and (101) surface plane structures pointed to the formation of different adsorbed species depending on crystal face atomic structure. The formation of different surface species correlated well with the acid-base strength of the coordinatively unsaturated atoms. This work has been accepted for publication in *Energy & Fuels*.¹

I also performed excited state DFT and post-Hartree-Fock calculations on small clusters. These calculations revealed that CO₂ does not undergo photoreduction on stoichiometric, defect-free anatase surfaces. On the other hand, the presence of surface oxygen vacancies may promote CO₂ photoreduction. Further work involves investigating the effects of lanthanide doping via periodic DFT calculations.

Experimental studies of lanthanide-doped TiO₂ photocatalysts

Studies by other researchers have shown the electron-hole recombination rates (a critical factor in influencing product quantum yields) in rare-earth-doped TiO₂ to be lower than that for undoped TiO₂. The role of lanthanide doping in creating active site states and mediating CO₂ photoreduction is currently unknown. 0-2.5% w/w La-doped TiO₂ catalysts were synthesized using a sol-gel process. Experiments using these catalysts in a continuous flow photoreactor showed that La-doped TiO₂ could mediate the photoreduction of CO₂ to methane. These catalysts were characterized using in situ electron paramagnetic resonance (EPR) spectroscopy and evidence for surface-trapped photo-generated electrons and holes on sol-gel TiO₂ was found. These studies showed that pulsed EPR spectroscopy can be used to study photo-induced processes in sol-gel TiO₂. Current work involves testing these catalysts in a medium-vacuum photoreaction system.

¹V.P. Indrakanti, J.D. Kubicki, H.H. Schobert, "Quantum chemical modeling of ground states of CO₂ chemisorbed on anatase (001), (010) and (101) TiO₂ surfaces", accepted for publication in *Energy & Fuels*.