ARTIFICIAL PHOTOSYTHESIS USING SEMICONDUCTOR NANOMATERIALS: APPLICATION OF TiO_2 NANOTUBES AND NANOWIRES IN PHOTOCATALYTIC CO_2 REDUCTION

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BACKGROUND

Photocatalytic CO_2 reduction and enhanced production of CH_4 and other light hydrocarbons using TiO_2 nanostructures

The conversion of CO_2 into value added fuels such as CH_4, C_2H_6, CH_3OH using solar energy by adopting sustainable and green chemistry approaches poses several challenges. Although nanotechnology and semiconductor catalysis has brought about several solutions, limitations remain in many aspects of the process that include: hydrocarbon product yield, control of the multistep electron-transfer process, use of broad spectrum sunlight, achievement of higher quantum efficiencies and reusability of the catalysts. Our group has been active in this research area and has achieved breakthroughs in vapor phase CO_2 reduction by developing novel semiconductor catalysts based on TiO_2 nanotubes. We used solution-processed (hence low cost and simple) semiconductor nanomaterials to solve existing issues with photocatalytic CO_2 reduction enabling enhancement in CH_4 yield. To-date, we achieved:

- Remarkable performance in photocatalytic CO_2 reduction to hydrocarbons by the use of ***Light Trapping Architectures***; Periodically modulated TiO_2 nanotubes (PMTiNTs) are bottom-up grown photonic crystals which have provided the highest performance thus far in stand-alone TiO_2-based photocatalysts
- Enhanced charge separation and lower recombination through ***built-in fields at Schottky-type heterojunctions*** formed by functionalization of the PMTiNTs with size controlled metallic and bimetallic nanoparticles [1 - 4]
- Enhanced CH_4 yield using transparent TiO_2 nanotubes (TNAs) functionalized with Au, Ru and ZnPd NPs [2]
- Enhanced harvesting of visible photons in the blue and violet spectral range using interfacial charge transfer states and sub-bandgap states [2, 3]

Considering our expertise in the field, we are in a position to develop novel approaches for photocatalytic CO_2 reduction to light hydrocarbons (i.e. CH_4, etc.) that can be adopted in practice.

SHORT-TERM OBJECTIVES

Apply our expertise in electrochemical anodization, electrodeposition, photodeposition, and microfabrication to synthesize novel photocatalysts based on TiO_2 nanostructures. Specifically, we plan to:

- Develop schemes for synthesizing exotic TiO_2 based nanostructures, for example, those with: tuned defect densities, varying nanoscale morphology, co-exposed crystalline facets, a mixture of crystalline phase content, etc.
- Facilitate enhancement of CO_2 photoreduction by functionalizing and/or doping the exotic TiO_2 nanostructures with visible light harvesting species.

Test the photocatalysts for CO_2 reduction performance:

- Design reactor and experimental setups to perform CO_2 reduction experiments in simulated solar light conditions
- Record hydrocarbon yield by CO_2 photocatalysis experiments
- Calculate quantum efficiency of catalysts
- Understand reaction mechanism and reaction intermediates
- Perform isotope ratio mass spectrometry, solid-state nuclear magnetic resonance spectrometry and electron paramagnetic resonance spectrometry to enhance our understanding of the underlying physical and chemical processes governing CO_2 reduction.

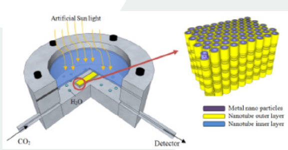

Figure 1: Schematic of reactor for photocatalytic CO2 photoreduction using TNAs

PROJECT OVERVIEW

Light trapping TiO_2 nanotube photonic crystals and high performance CO_2 photoreduction using periodic modulation of the nanotube diameter

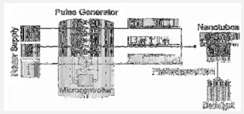

Figure 2: Process flow for PMTNTs synthesis [1]

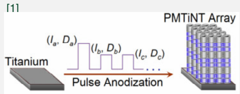

Figure 3: Anodization process for formation of PMTiNTs [1]

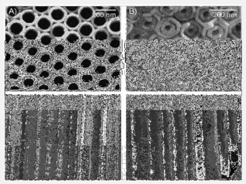

Figure 4: FESEM images for the periodically modulated TiO2 nanotubes [1]

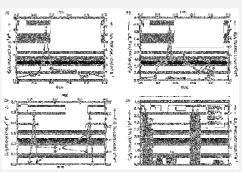

Figure 5: Photocatalytic CH_4 by CO_2 reduction using periodically modulated TiO_2 nanotubes [1]

Enhanced CH_4 production by CO_2 photoreduction using photodeposted Au, Ru and ZnPd nanoparticles on TiO_2 nanotubes

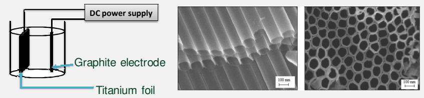

Figure 6: Anodization experimental setup schematic (left); and FESEM images of TiO_2 nanotubes grown on FTO (middle and right); [2]

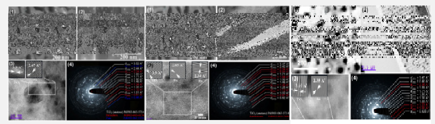

Figure 7: FESEM, TEM images and TEM dot pattern of Au (right) nanoparticles deposited on transparent TiO_2 nanotubes [2]

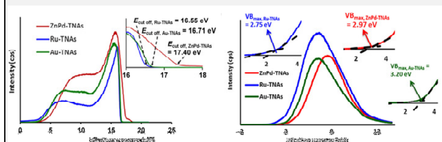

Figure 8: Ultraviolet photoelectron spectroscopy (UPS) work-function spectra (left) and UPS valence spectra of ZnPd incorporated TiO_2 nanotubes (ZnPd-TNAs), Ru incorporated TiO_2 nanotubes (Ru-TNAs) and Au incorporated TiO_2 (Au-TNAs) [2]

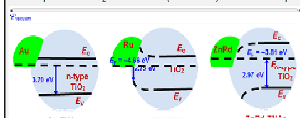

Figure 9: Band diagram of Au-TNAs, Ru-TNAs and ZnPd-TNAs [2]

Table:- CH4 yield

Catalyst	CH_4 yield (µmol·g⁻¹·h⁻¹)
Au-TNAs	58.47
Ru-TNAs	26.37
ZnPd-TNAs	[illegible]

Interfacial electric field between metal nanoparticles TiO_2 nanotubes

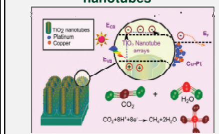

Figure 10: Band diagram of CuPt incorporated TiO_2 nanotubes (CuPt-TNAs)

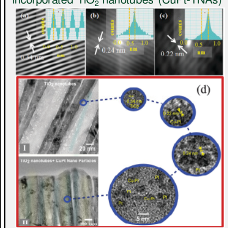

Figure 11:Transmission electron microscope (TEM) images of CuPt-TNAs [3]

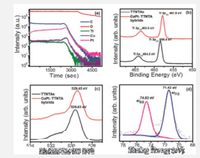

Figure 12: TOF-SIMS and XPS data of CuPt-TNAs [3]

Conclusion:

- TiO_2 nanostructures have been applied in the photocatalytic reduction of CO_2 to light hydrocarbons
- Our group has attained remarkable success in the field and aims for even bigger outcomes in the field of photocatalytic CO_2 reduction to hydrocarbons
- We aim to leverage our expertise in solution-processed nanomaterial synthesis and experimental setup for CO_2 reduction take the technology further by performing further experiments on new catalysts
- In addition we aim to leverage our expertise in performing fundamental studies to understand the mechanism(s) of photocatalytic CO_2 reduction

THEME OVERVIEW

Solar

The sun powers the entire world, providing warmth, light, and sustenance for countless forms of life. Technologies have made it possible to use some of the sun's energy to produce electricity and fuels, but new refinements may allow us to diversify the ways in which solar energy can be generated, stored, and utilized. By identifying lower-cost materials for use in the construction of solar cells, finding new catalysts to enable different types of production, identifying more efficient methods for market integration, and considering the possibility of solar-derived hydrogen fuels, it may be possible to develop vast energy resources from the most abundant source in our lives.

EXPECTED OUTCOMES

1. ***Energy Harvesting***: This project will advance the science and technology of visible light driven photocatalysts. Materials and Devices to harvest Canada's abundant supply of solar energy is an anticipated outcome in the longer term.
2. ***Energy Storage***: The conversion of CO_2 into portable solar fuels converts solar energy into that present in chemical bonds, and avoids the intermittency problem of photovoltaics.
3. ***Reducing the Use of Expensive Noble Metals***: The best photocatalysts currently use non-negligible amounts of Au, Pt or Pd. Bimetallic base metal-noble metal structure-controlled nanoparticles are expected to greatly reduce the usage of noble metals and bring down costs.
4. ***Lowering Carbon Footprint***: CO_2 photoreduction, whether under natural sunlight or under artificial illumination, presents a very environmentally friendly and potentially cost-effective method to reduce/offset CO_2 emissions (for instance at coal-fired power plants) and also generate carbon credits.
5. ***New Electronic Materials***: Novel semiconductors and heterojunctions expected to be synthesized in this project will likely have applications in sensors, light emission, industrial catalysis, etc.
6. ***HQP Training***: A new cadre of Canadian researchers in emerging areas such as photovoltaics, nanotechnology and materials science will be created.

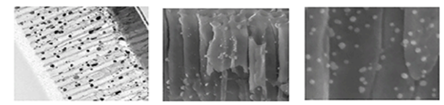

Figure 13: FESEM images of Au-TNAs, Ru-TNAs and ZnPd-TNAs

Publications from our group:

[1] X. Zhang et al, "Photocatalytic conversion of diluted CO_2 into light hydrocarbons using periodically modulated multiwalled nanotube arrays" *Angewandte Chemie* 124, no. 51 (2012): 12904-12907

[2] P. Kar, et al,"Enhanced CH_4 yield by photocatalytic CO2 reduction using TiO_2 nanotube arrays grafted with Au, Ru, and ZnPd nanoparticles" *Nano Research* 9, no. 11 (2016): 3478-3493.

[3] S Farsinezhad et al, "Interfacial band alignment for photocatalytic charge separation in TiO_2 nanotube arrays coated with CuPt nanoparticles" *Physical Chemistry Chemical Physics* 17, no. 44 (2015): 29723-29733.

[4] B. Amirsolaimani et al, Effect of the nature of the metal co-catalyst on CO_2 photo-reduction using fast-grown periodically modulated titanium dioxide nanotube arrays (PMTiNTs)." *MRS Online Proceedings Library Archive* 1578 (2013).

EXTERNAL PARTNERS

1. **Technical University of Munich** (NSERC Create Grant): We are working with the Thomas Nilges Group on new visible absorbing semiconductors, and with the Müller-Buschbaum group on new solar energy harvesting configurations.
2. **University of Bayreuth**: We are working with the Panzer group on fundamental optoelectronic measurements in single crystal halide perovskites.
3. **NRC-NINT**: Advance photocatalysts and photovoltaics using earth abundant semiconductors. We are actively collaborating with Drs. Alex Kobryn and Sergey Gusarov on DFT, MD and RISM modeling of TiO2-based and perovskite-based nanomaterials.
4. **Shastri Indo-Canadian Institute**: We have a funded collaboration on TiO_2 nanomaterials with the Roy Group in Physics at the Indian Institute of Technology-Madras.
5. **Shankar Group** graduate students have received $14,000 in nanofab usage vouchers from CMC Microsystems for research projects on nanomaterials and nanodevices.

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