ARTIFICIAL PHOTOSYTHESIS USING SEMICONDUCTOR NANOMATERIALS: CHALCOGENIDE SEMICONDUCTOR NANOMATERIALS FOR PHOTOCATALYSIS APPLICATION

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BACKGROUND

INTRODUCTION

There is rejuvenated interest, worldwide, in chalcogenide based semiconductor nanomaterials for solar light harvesting, particularly for photocatalysis applications. Chalcogenide semiconductor nanostructures are technologically interesting because of their advantages over the existing state-of-the-art materials due to their generally low bandgap, which can be easily tuned by varying their stoichiometry. Chalcogenide nanomaterials readily exhibit quantum confinement due to the moderate-to-large values of the Bohr exciton radius in them. Degenerately doped chalcogenides (e.g. Cu_2S and CuS) localized surface plasmon resonance (LSPR) at near-infrared wavelength. Some chalcogenide nanomaterials have exhibited simultaneous excitonic and plasmonic resonances.

The development of processing methodologies to synthesize chalcogenide nanomaterials remains a major challenge to researchers, when it comes to achieving control over the properties of interest from the standpoint of photocatalytic performance which are: nanoscale morphology, crystalline phase content, and crystallographic texture. Research efforts have been ongoing in our group on development of new chalcogenide semiconductor nanostructures for solar energy harvesting [Ref 1 and Ref 2].

SHORT-TERM OBJECTIVES

DEVELOPMENT OF NOVEL CHALCOGENIDE MATERIALS

- Apply our expertise in solution-processing (i.e. electrochemical anodization, electrodeposition, etc.) to develop and synthesize new chalcogenide semiconductor nanomaterials
- Investigate photocatalytic performance of the newly developed materials
- Perform advanced characterizations of the chalcogenide nanomaterials in order to probe their optoelectronic properties

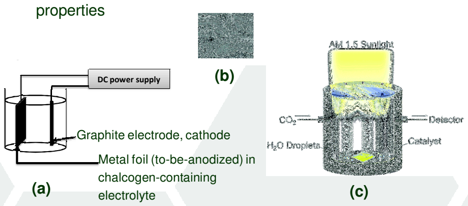

Fig. 1: Sequence of steps from materials synthesis (a) to CO_2 reduction experiments (c) : (a) Experimental set-up for anodization, (b) Chalcogenide nanostructure, and (c) Typical experimental setup for photocatalytic CO_2 reduction using copper sulfide (Cu_2S and CuS) nanostructures.

PROJECT OVERVIEW

Anodic copper sulfide (Cu_2S and CuS) nanostructures: Our group has been successful in synthesizing vertically oriented copper sulfide nanostructures by a simple, scalable and low cost solution processing (i.e. electrochemical anodization) route [1] and we aim to continue applying our expertise to develop novel binary and ternary chalcogenide materials of similar types for applications in photocatalysis. Copper sulfides are chalcogenide semiconductors with a suitable band-gap between 1.21 and 2 eV, and they have a room-temperature hole-mobility of ~ 1 cm^2/V-s. These nanomaterials demonstrated promising performance as stand-alone catalysts for CO_2 photoreduction, generating 38 μmol m^{-2} h^{-1} under AM1.5 one sun illumination [1].

Electrodeposited CdTe on rutile TiO_2 nanowires: We synthesized both *n*-type and *p*-type CdTe by a simple two-electrode electrodeposition process onto rutile TiO_2 nanowires (NWs), whereby we formed a photovoltaic solar cell [2]. We plan to use engineered CdTe thin films and nanostructures for applications in high performance photocatalysis.

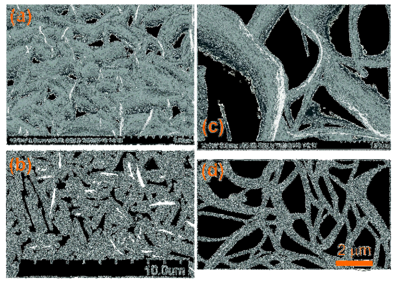

Fig. 2: FESEM images of copper sulphide nanostructures, formed at: (a) 1.5 V, (b) 3 V, (c) 1.5 V, and (d) 1.5 V [1]

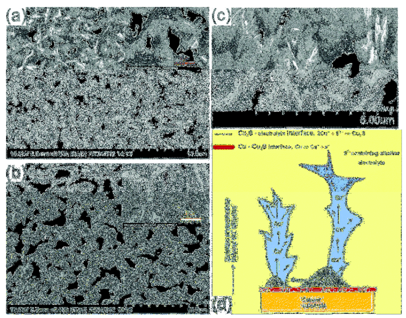

Fig. 3: FESEM images of copper sulfide nanostructures, formed at: (a) 4 V, ((b and (c)) 8 V. (d) is the growth mechanism [1]

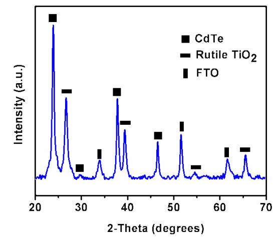

Fig. 4: XRD pattern of CdTe deposited TiO_2 NWs showing the presence of CdTe as well as rutile phase TiO_2. XRD pattern is consistent with TEM fringe pattern (shown below) [2]

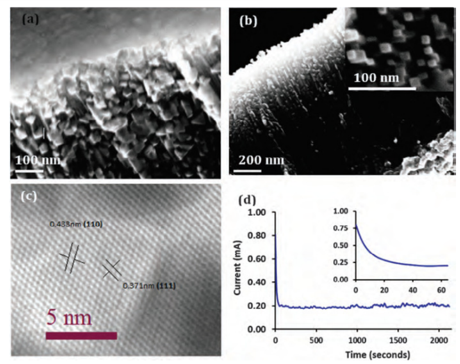

Fig. 5: (a and b) are the cross-section FESEM images (c) is the TEM lattice image and (d) is the current transient of the CdTe electrodeposition process of the CdTe coated TiO_2 NWs [2]

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

CHALCOGENIDE MATERIALS BASED TECHNOLOGIES FOR PHOTOCATALYSIS

- Synthesis of new types of chalcogenide semiconductor nanomaterials using simple solution-processed methods – these may include materials such as: binary and ternary chalcogenides semiconductor nanomaterials, e.g. CuZnS, CuZnTe, etc.; and chalcogenide perovskites, e.g. $AB(O_{1-x}S_x)$, where A and B and metals
- An understanding of nanoscale characteristics of the chalcogenide semiconductor nanomaterials, via advanced characterization methods
- Measurement of photocatalytic performance and their dependability on chalcogenide semiconductor nanomaterials' characteristics and processing conditions
- Methodologies to improve/enhance photocatalytic performance using low cost and efficient catalysts made of chalcogenide semiconductor nanomaterials

PUBLISHED WORK FROM OUR GROUP

[1] P. Kar, S. Farinezhad, X. Zhang, and K. Shankar "Anodic Cu_2S and CuS nanorod and nanowall arrays: preparation, properties and application in CO_2 photoreduction", *Nanoscale* - RSC, 2014, 6 (23), 14305-14318 (**cited 34 times to date**).

[2] A. Hosseini, P. Kar, H. Ling-Hsuan, S. Farinezhad, b. Wiltshire, A. Mohammadour, Y. Zhang, and K. Shankar, "Radial Heterojunction Solar Cell Consisting of n-Type Rutile Nanowire Arrays Infiltrated by *p*-Type CdTe" *J. Nanoscience & Nanotechnology*, 2017, 17, pp. 1–5

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: Advancing research into 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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