2011 DOE Hydrogen and Fuel Cells Program Review

USD Catalysis Group for Alternative Energy

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The University of South Dakota

May 10, 2011
Project ID #: PD078

Overview

Timeline

Start: 12/01/2009
End: 11/30/2011
Completion: 65%

Budget

DOE share: $1,046,650
FY10: $0
FY11: $0
Contractor share: $261,666

Partners

University of South Dakota
South Dakota School of Mines & Technology
Argonne National Laboratory

Barriers Addressed:

DOE Fuel Cells Technology Program Multi-year Research, Development, and Demonstration Plan 2005-2015 / Technical Plan 2007:

Hydrogen Production:

1. Technical Objective, ‘Develop advanced renewable photoelectrochemical and biological hydrogen generation technologies. By 2018, verify the feasibility of these technologies to be competitive in the long term.’

Approaches include:
- Develop high-efficiency PEC materials
- Improve durability of materials
- Identify functional requirements and develop auxiliary device and systems materials
- Develop PEC devices and systems

2. Technical Objective, H_2 Separation.

Fuel Cells:

3. Technical Objective: Develop more efficient, lower cost H2 fuel cells. For example, ‘By 2010, develop a 60% peak-efficient, durable, direct hydrogen fuel cell power system for transportation at a cost of $45/kW; by 2015, a cost of $30/kW.

Approaches include:

Electrodes:
- Develop supports with reduced corrosion
- Optimize electrode design and assembly, including design of scaleable, high-throughput fabrication processes and optimization of catalyst / support interactions and microstructure.

Membrane-electrode assemblies:
- Expand the operating range of MEAs
- Test, analyze and characterize MEAs before, during, and after operation.

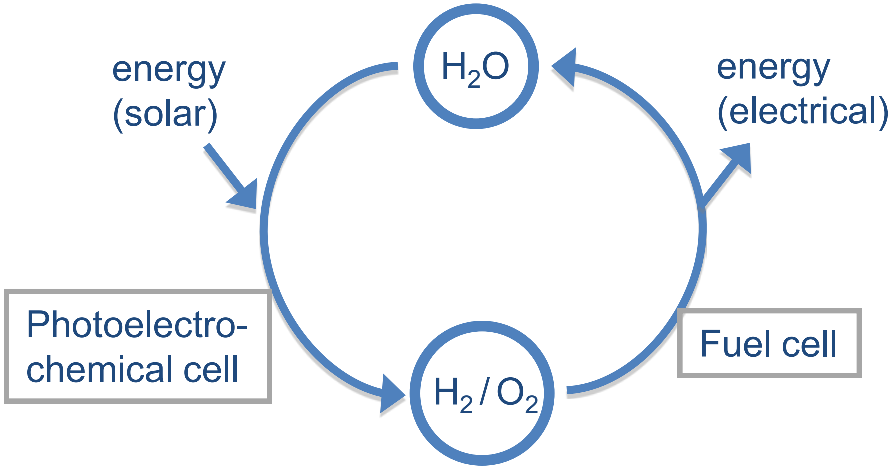
Relevance

Project Objective: The South Dakota Catalysis Group (SDCG) is a collaborative project with mission to develop advanced catalysts for energy conversion with two primary goals:

1) develop photocatalytic systems in which polyfunctionalized TiO_2 are the basis for hydrogen/oxygen synthesis from water and sunlight (solar fuels group)

2) develop new materials for hydrogen utilization in fuel cells (fuel cell group).

In tandem, these technologies complete a closed chemical cycle with zero emissions.



energy (solar)

H_2O

energy (electrical)

Photoelectro-chemical cell

H_2/O_2

Fuel cell

- Utilize solar energy
- Carbon neutral
- Catalysis will have a central role
- Water oxidation is a critical component

Relevance

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Proposal Objectives:

Task 1.0 [Photocatalysis]
Develop the methodology for the synthesis of highly functionalized nanostructures, incorporation into thin films, deposition of thin films onto capillaries, and fabrication of a prototype capillary reactor for photocatalytic water splitting using visible light.

Subtask 1.1 [Synthesis of inorganic photocatalyst]
Synthesize inorganic photocatalyst materials that incorporate semiconductor nanorods.

Subtask 1.2 [Develop nanorod thin films]
Use Langmuir-Blodgett (LB) methods to incorporate nanorods as membrane-spanning units to form thin films.

Subtask 1.3 [Develop and test a prototype capillary reactor]
Deposit nanorod thin films onto capillary supports that will be assembled to produce a prototype capillary reactor. The PEC materials and reactors developed will be tested using standard PEC testing protocols.

Task 2.0 [Fuell Cell Catalysis]
Develop fuel cell prototypes that exhibit high activity and long lifetime.

Subtask 2.1 [Synthesize Carbon Nanofelt]
Synthesize electrospun carbon nanofibers with novel morphological properties, including surface areas up to 2200 m^2/g, high graphitic crystallinity, diameters of 10-1000 nm, and pore diameters of 1-10 nm. The nanofibers will be woven into a mesh as component for the fuel cell.

Subtask 2.2 [Synthesize Nanocrystal Catalyst]
Metallic nanocrystals active as hydrogen fuel cell catalysts will be synthesized, with particular attention to control of particle morphology.

Subtask 2.3 [Develop and test prototype fuel cell]
In this task, catalyst nanocrystals will be deposited on carbon nanofelt as the active component of a fuel cell. Prototypes will be fabricated and tested with a laboratory fuel cell test station. Also, fundamental studies on the oxidation of the carbon support in a fuel cell environment will be carried out.

Approach

The solar fuels component of the project is centered on the use of high surface area TiO_2 decorated with functional components on the surface, including visible-NIR chromophores and catalysts. High surface area TiO_2 supports include aerogels, ordered mesoporous materials, nanotube arrays, and nanorods. As a prerequisite, the semiconductor support must present band-edge potentials that allow electron transfer steps ultimately to the component half-reactions for fuel and oxidant synthesis. Highly crystalline anisotropic nanocrystals of TiO_2, in particular, fulfill several requirements for a solar fuel catalyst. On the surface of the semiconductor, the chromophore enables absorption of a solar photon and exciton formation. Nearby catalyst centers on the TiO_2 surface must catalyze component half-reactions for fuel and oxidant synthesis. In a concerted cycle of electron-transfer steps, the exciton becomes separated. Electrons are collected and consumed at the fuel synthesis catalyst while the oxidant synthesis catalytic step results in donation of an electron back to the chromophore.

Electron-transfer steps at interfaces are fundamentally important in the solar catalysis process, and design of the material is critical in order to minimize bottlenecks. Several features of the photocatalyst affect electron-transfer rates, including covalent attachment of a chromophore, parity of energy levels of the chromophore, support, and catalyst, and size and morphology of the material. Furthermore, hierarchical organization of the nanoscale photocatalyst is required to realize the full potential of photocatalysis, such as scale-up and separation of fuel and oxidant.

Planned Milestones:

Synthesis of nanostructured material
  anisotropic TiO_2 nanocrystals
  catalyst nanocrystals

Organization of nanostructured material
  ordered mesoporous materials
  self-assembly

Catalyst evaluation
  spectroscopic characterization
  H_2 / O_2 evolution

Approach

The fuel cell component of the project is centered on improving the stability and performance of the support in hydrogen (and potentially other fuels) fuel cells. The lifetime of a fuel cell may be limited by the integrity of the support material, which may deteriorate during operation.

Fuel cell supports must be extremely robust and have high surface area. Other desirable features include tunable composition and morphology, low-cost and easy scale-up for production.

Electrospun fibers can potential satisfy many demands for fuel cell support material. The fibers can be electrospun from polymers and/or metal containing precursors, so there is autonomy within the method to alter the composition of the material. The electrospun fibers can be synthesized under varied conditions that affect morphological properties, such as diameter (typically 10-100 nm) or even inclusion of pores. Thermal treatment of electrospun fibers, as an added processing step, can yield graphitized fibers, ceramic fibers, metal carbide fibers, for example. Finally, the nanofibers can be woven to produce nanofelts.

The nanofelt is hierarchical in nature, with morphological control at the nanoscale, microscale, and macroscale. Optimized materials composition and morphology can potentially lead to significant performance advantages in the working fuel cell environment.

Planned Milestones:

Electrospun Fibers
  electrospun polymer fibers
  electrospun ceramic fibers

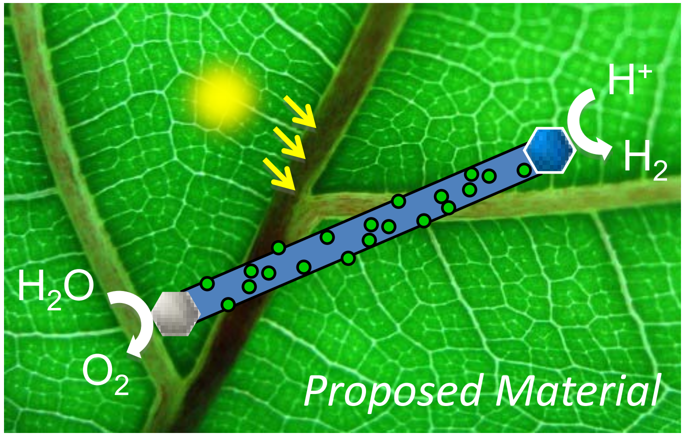
Fuel cell supports
  graphitization of carbonaceous fibers
  woven nanofelts

Fabricate MEA

Fuel cell performance evaluation

Graphite edge chemistry
  spectroscopic investigation
  catalysis
  stability

Technical Accomplishments and Progress



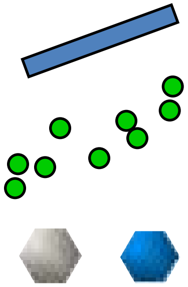
Dye-sensitized TiO_2 nanorod with catalyst particle tips:

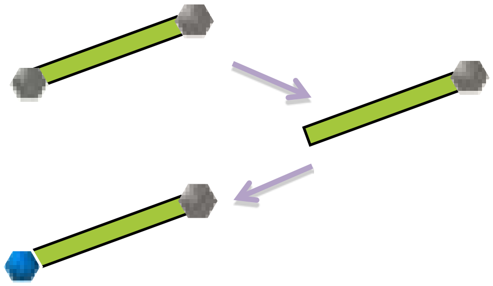
- efficient charge transport along the nanorod
- sensitization for efficient visible light absorption
- catalyst particles attached

1) TiO_2 nanorod

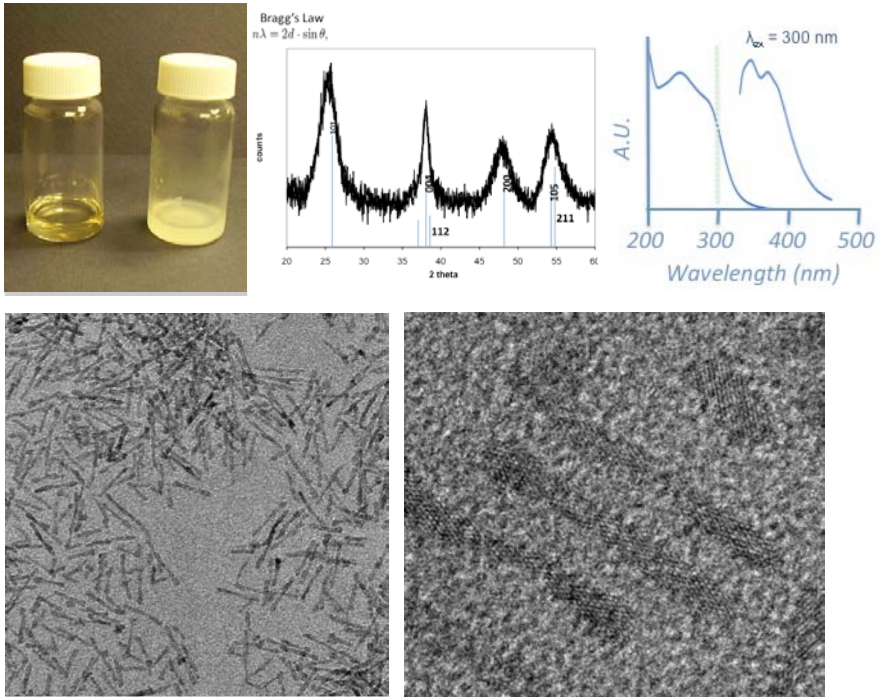
2) sensitization

1) addition of catalysts to tips

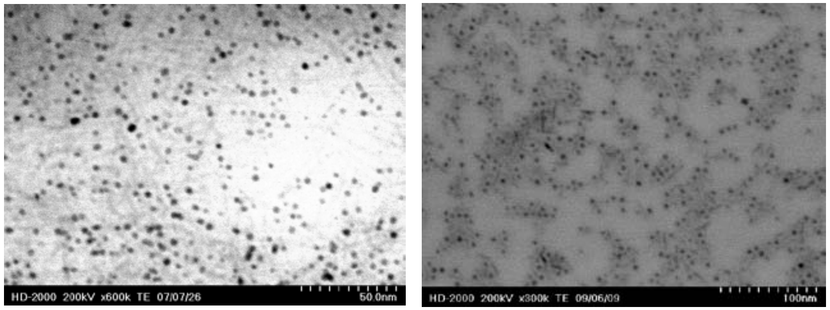




TiO_2 nanorod synthesis and characterization:
Optical image, powder XRD, UV-visible absorbance and emission, TEM

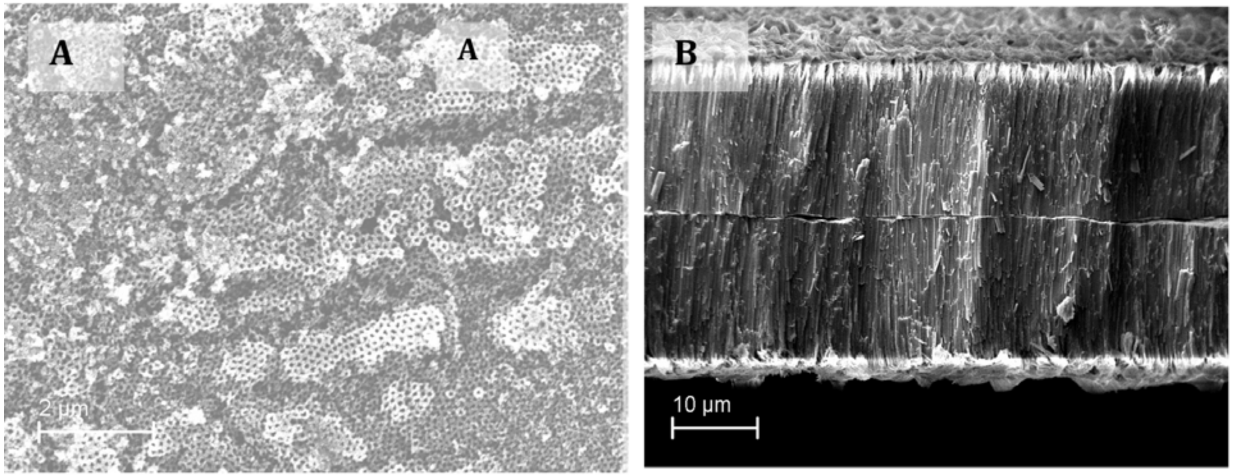


Nucleation of Pt (left) or Co (right) in the presence of TiO_2 nanords:
(attachment on tips not yet achieved)



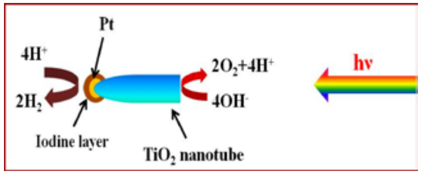
Technical Accomplishments and Progress

Anodized Ti foil: double layer of ordered TiO_2 tubes

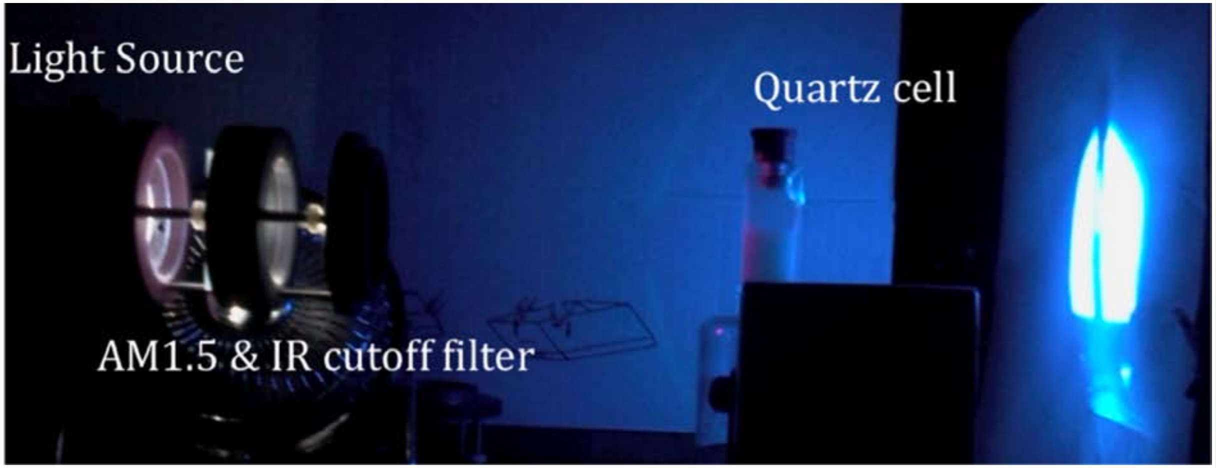


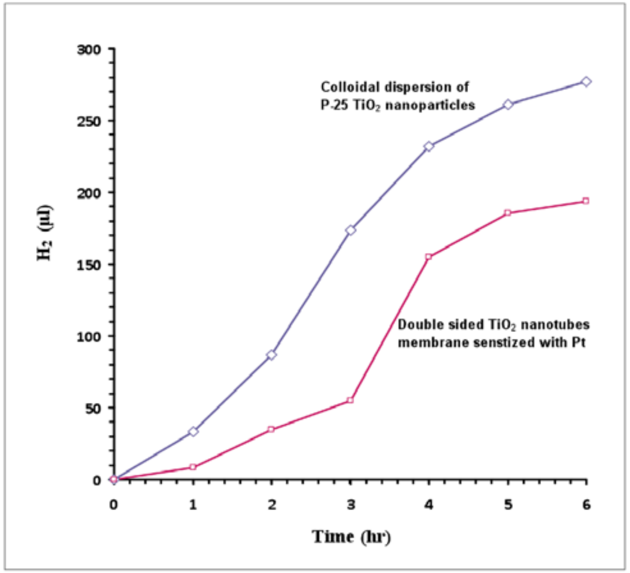
The double-membrane was impregnated with H_2PtCl_6, and calcined under reducing conditions.

Photocatalysis:
10% methanol in water
500 W Xe lamp with filter
(220 < λ < 400 nm transmitted)



Photocatalysis and H_2 generation

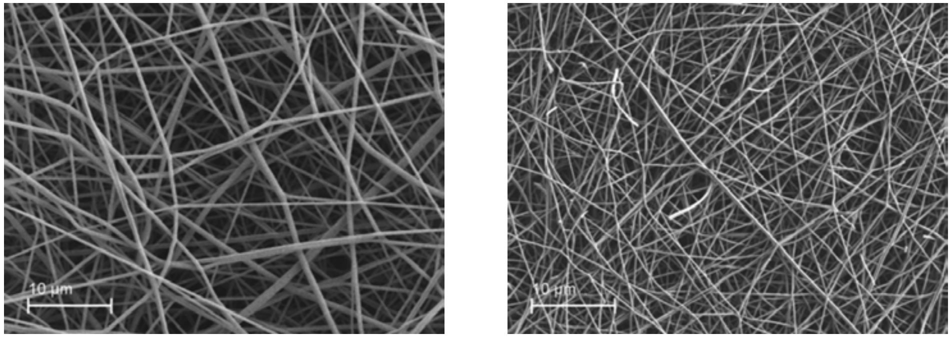




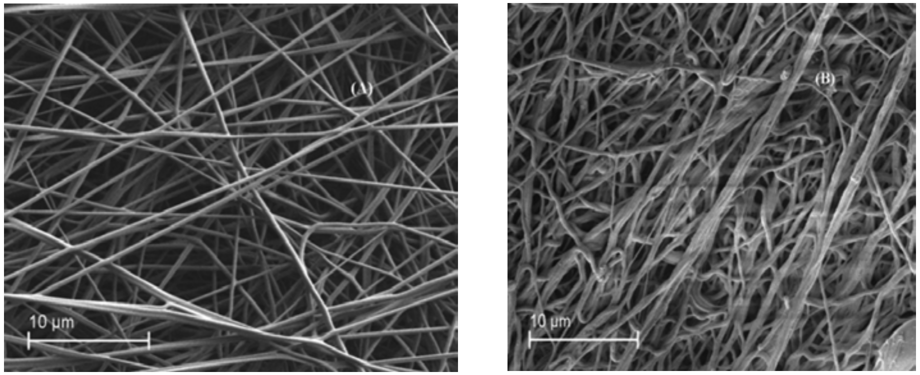
Technical Accomplishments and Progress

Electrospun polymer fibers are precursors for carbon nanofibers

Polyacrylonitrile fibers → carbon nanofibers



Polyvinylalcohol fibers → carbon nanofibers



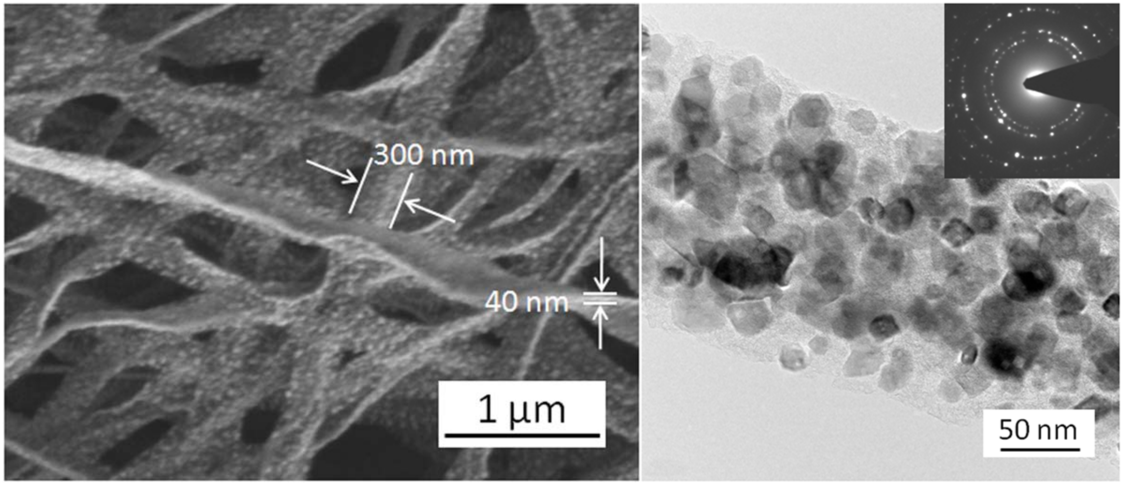
Conditions during electrospinning affect morphology of the polymer fibers (diameter, porosity)

Thermal treatment leads to carbon nanofibers (graphitization occurs at higher temperatures with retention of morphology)

High surface area (up to 2200 m^2/g)

Technical Accomplishments and Progress

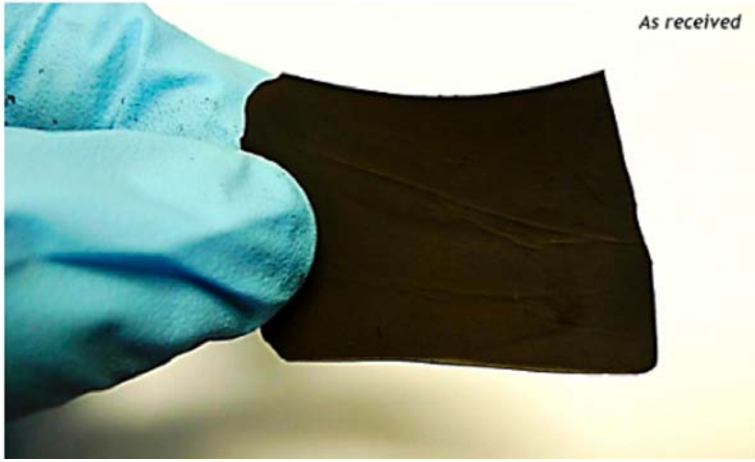
TiC nanoribbons

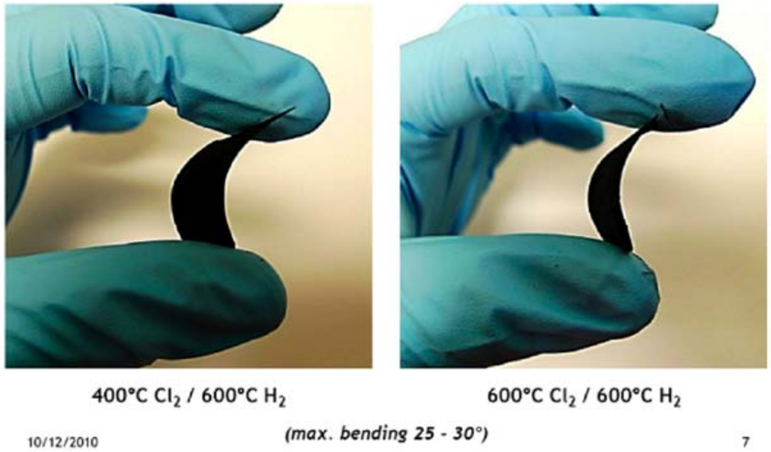


Continuous titanium carbide (TiC) nanofibers possess nanoribbon morphology with width and thickness being ~300 nm and ~40 nm, respectively, and contained TiC crystallites with sizes ranging from 5 nm to 30 nm were synthesized through electrospinning followed by carbothermal reduction.

Removal of Ti leads to carbide-derived carbon with exceptionally large pore volume and surface area.

TiC nanofelt → carbide-derived carbon





400°C Cl_2 / 600°C H_2

600°C Cl_2 / 600°C H_2

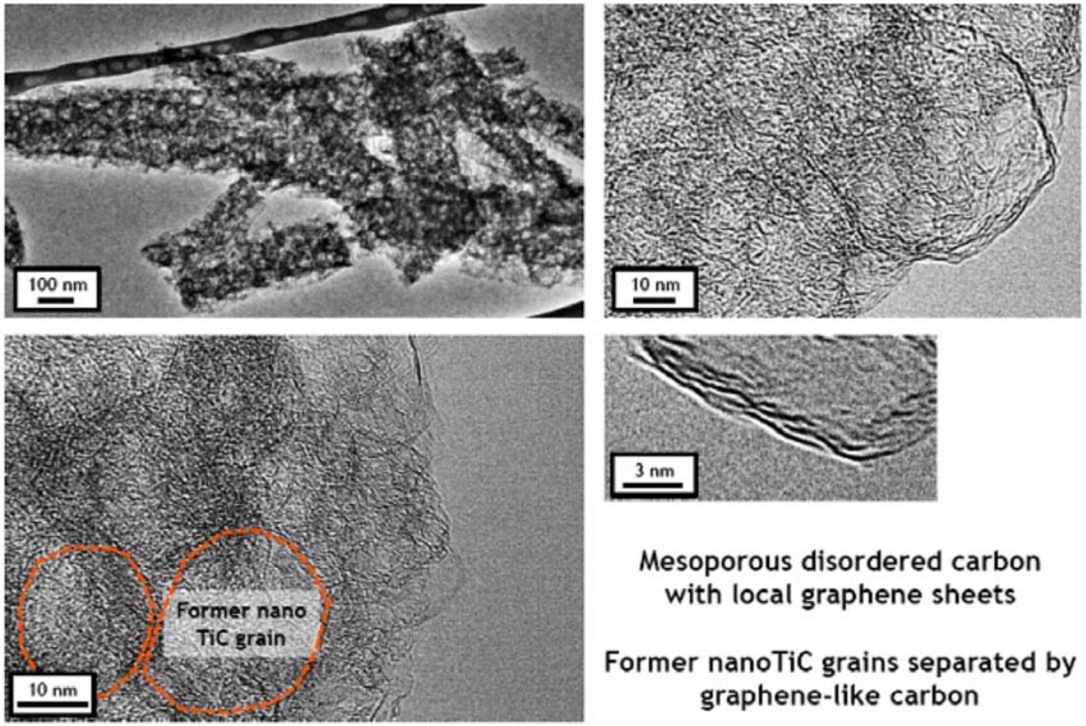
(max. bending 25 - 30°)

10/12/2010

7

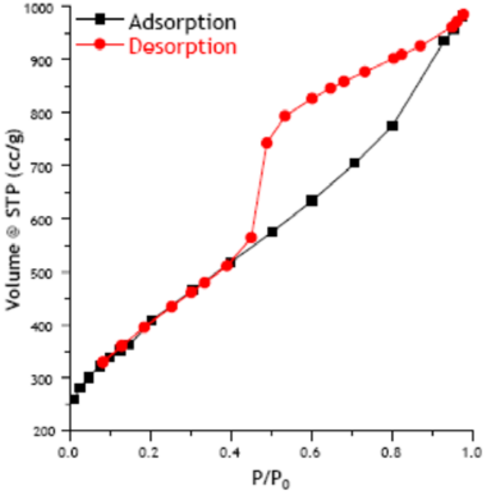
Technical Accomplishments and Progress

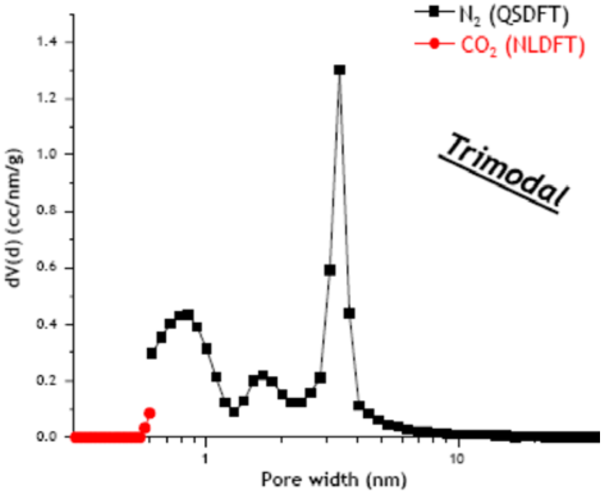
CDC nanofibers have disordered poly-graphene structure



Mesoporous disordered carbon with local graphene sheets

Former nanoTiC grains separated by graphene-like carbon



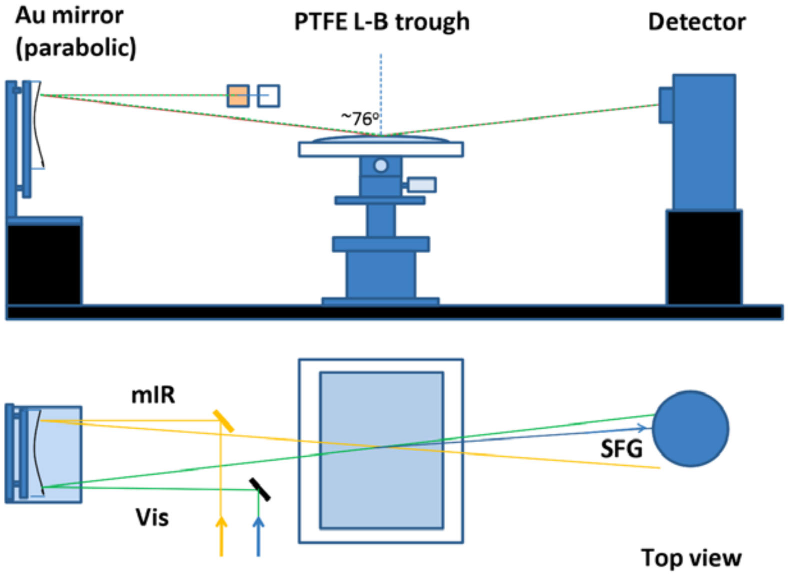


BET Surface area = 1390 m^2/g
Pore volume = 1.51 cm^3/g
Mean width = 1.6 nm

Technical Accomplishments and Progress

Equipment acquisition:

KSV-2000 Langmuir-Blodgett trough
High temperature graphitization furnace
Vibrational sum-frequency generation capabilities



Collaborations

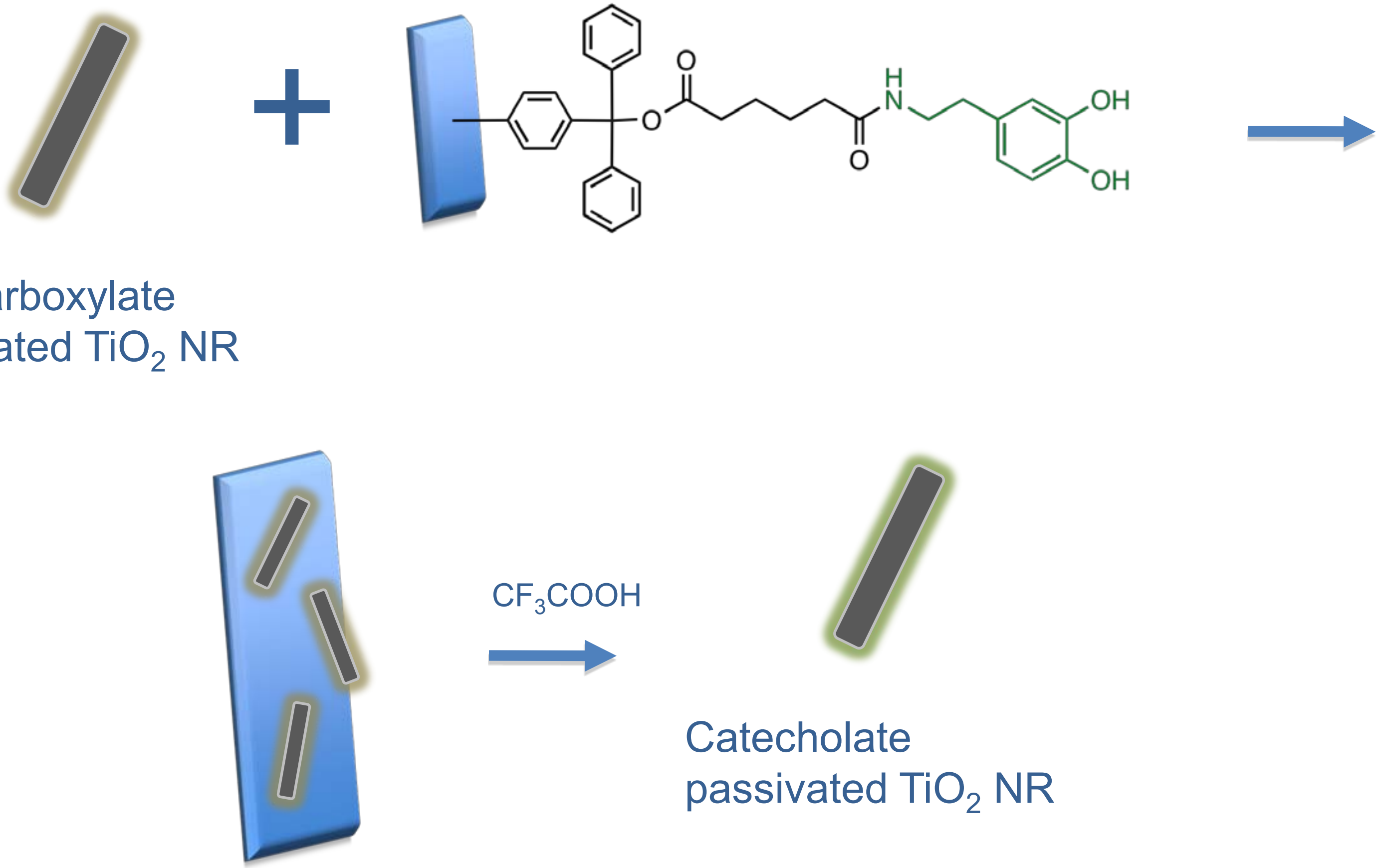
The University of South Dakota
- James Hoefelmeyer
- Ranjit Koodali
- Grigoriy Sereda
- Dan Engebretson

South Dakota School of Mines & Technology
- Jan Puszynski
- Hao Fong
- Rajesh Shende
- P.S. Ahrenkiel
- Jacek Swiatkiewicz

U.S. Department of Energy
- Hydrogen and Fuel Cells Program
- Argonne National Laboratory

Proposed Future Work

Catecholate groups on TiO_2 NR



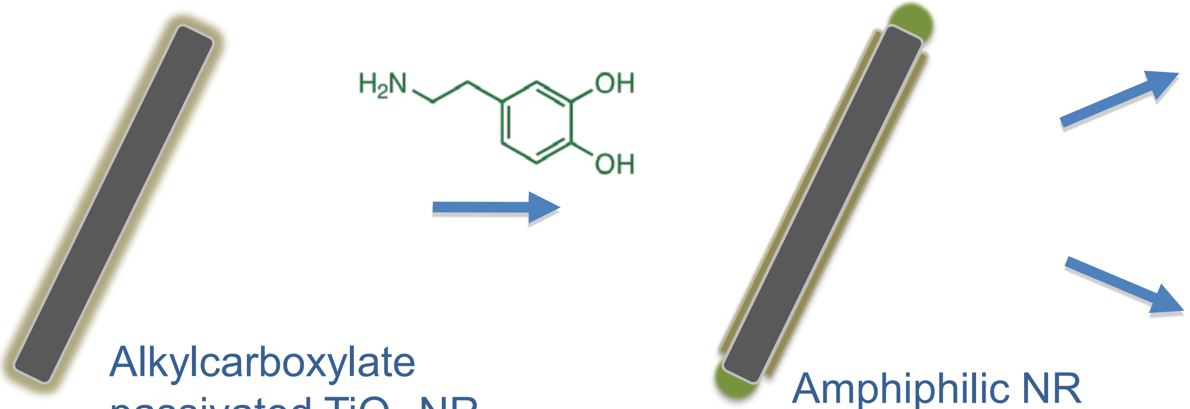
Alkylcarboxylate
passivated TiO_2 NR

CF_3COOH

Catecholate
passivated TiO_2 NR

Proposed Future Work

Toward Amphiphilic Nanorods

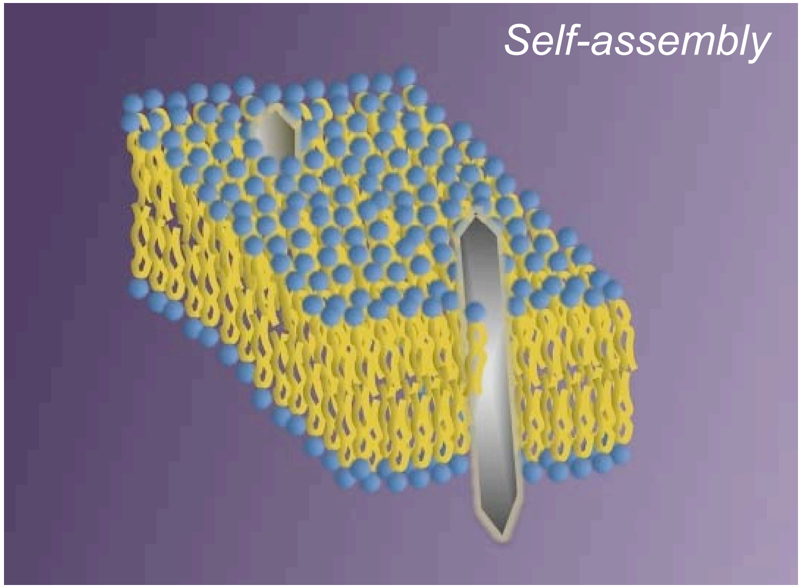


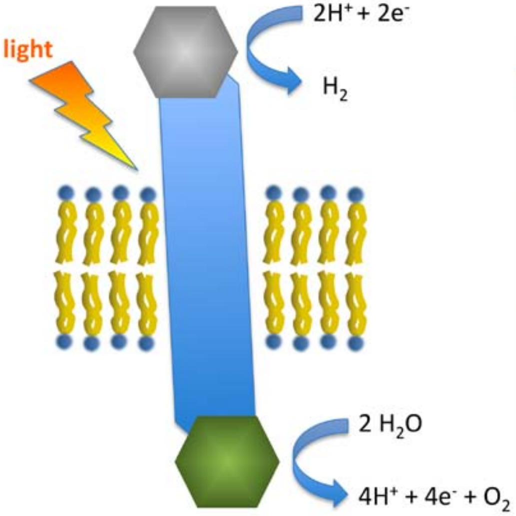
Alkylcarboxylate
passivated TiO_2 NR

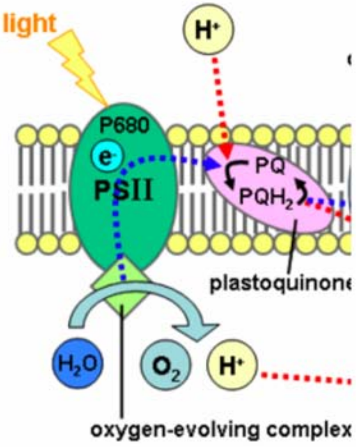
Amphiphilic NR

Self-assembly
(with lipids)

Nucleation of
metals on tips







Summary

- The SDCG addresses research challenges in PECs and Fuel Cells, and is building research infrastructure in SD

- The PEC group uses three types of nanostructured TiO_2 (nanorods, nanotube arrays, and mesoporous materials). The group is in the process of developing surface modification procedures (sensitization, catalyst addition).

- The Fuel Cells group uses the technique of electrospinning to produce polymer nanofibers. The fibers are precursors for carbon or ceramic nanofibers. Metal-carbide fibers have been used to make carbide-derived carbon. Nanofibers can be woven into nanofelts that offer ideal properties as supports for fuel cells.

- Future work will focus on evaluation of performance of nanofelts in working fuel cell environment, synthesis of surface modified TiO_2 nanostructured materials, self-assembly of TiO_2 nanorods in thin films, and PEC fabrication and testing.