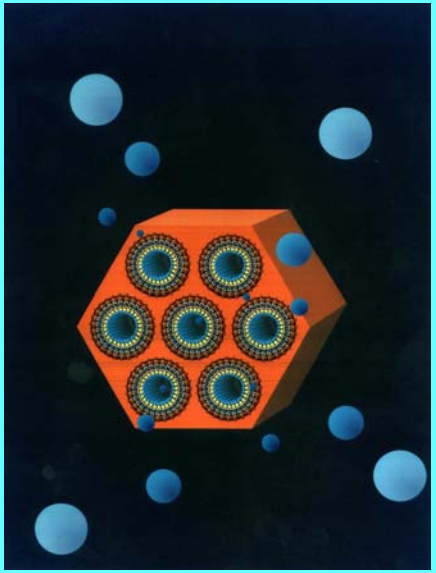
Nanoscience and Nanotechnology Initiative

Synthesis and Characterization of Hybrid Nanostructured Organic-Inorganic Electrodes



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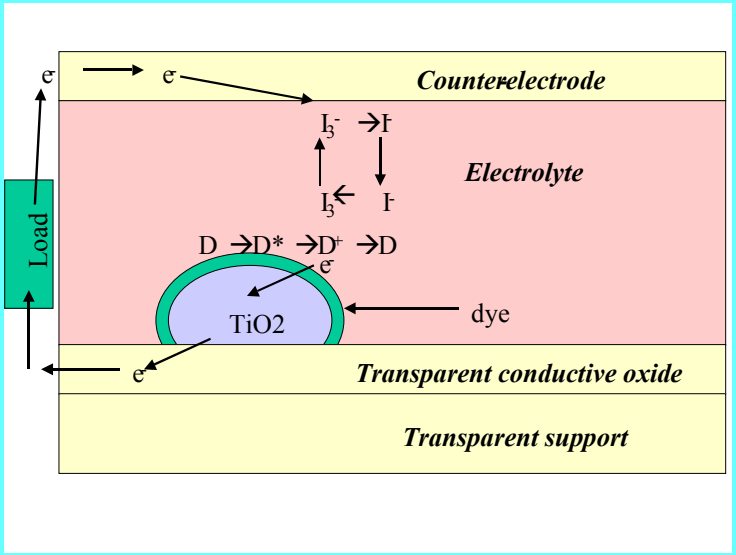
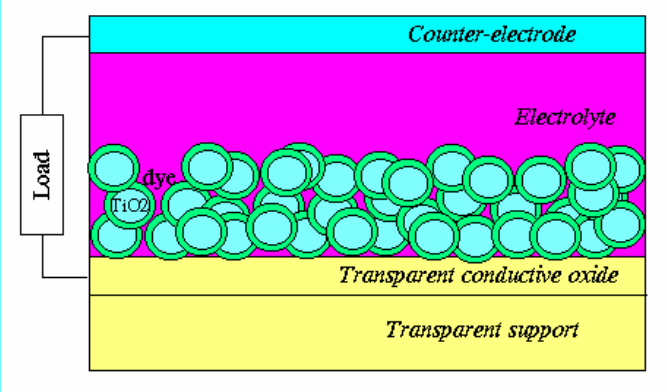
Technical Objective

- Control the geometry and chemistry of NOIS electrodes
- Understand the dependence of exciton generation, dissociation and geminate recombination in NOIS electrodes as a function of systematically controlled inorganic nanostructure, interfacial architecture and organic thin film chemistry

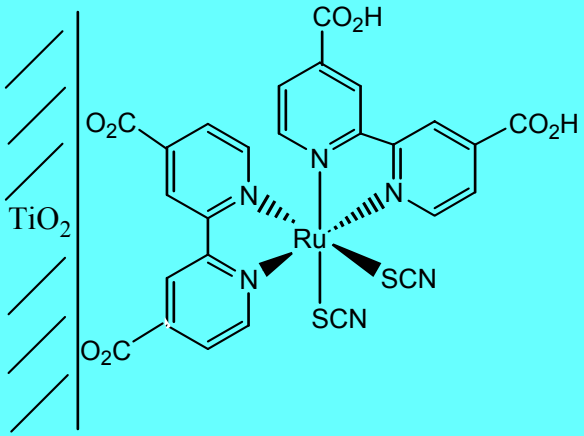


Background

- **State-of-the-Art today**
  Solar cells with 11% conversion efficiency
  Electrochromic displays with 100 ms response
  Electrodes made by sintering TiO_2 particles



- **Problems…**
  High efficiency solar cells need liquid electrolyte
  Response time needs improvement for display applications
  Poor control over fabrication of NOIS electrodes
  Limited surface area and irregular pore structure
  Back electron transfer

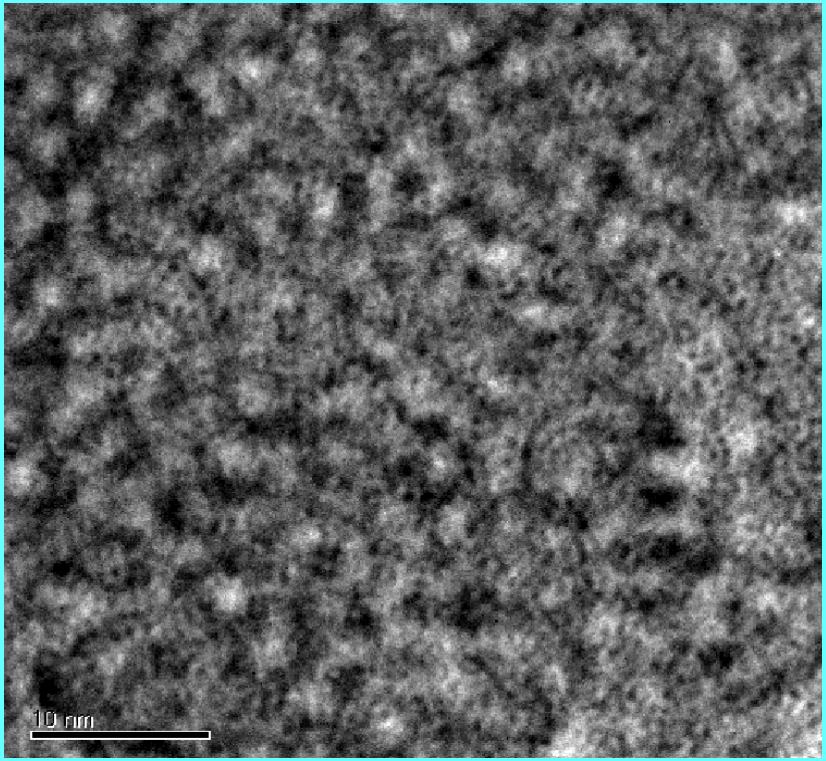


Technical Challenges

- Nanoporous transition metal oxides can be challenging structures to prepare since they tend to be thermally unstable resulting in mesopore collapse and loss of surface area during calcination.
- Need a low temperature surfactant-templated deposition techniques to make high surface area nanoporous titania thin films.
- Need an effective, low temperature method for removing the surfactant template
- Need a novel method for stabilizing titania nanocrystallites within the mesostructured greenbody to prevent structural collapse.
- Need more effective modes of dye incorporation to maximize dye content and minimize back electron transfer.
- Need to maintain open pore structure to speed diffusion, improve response time.

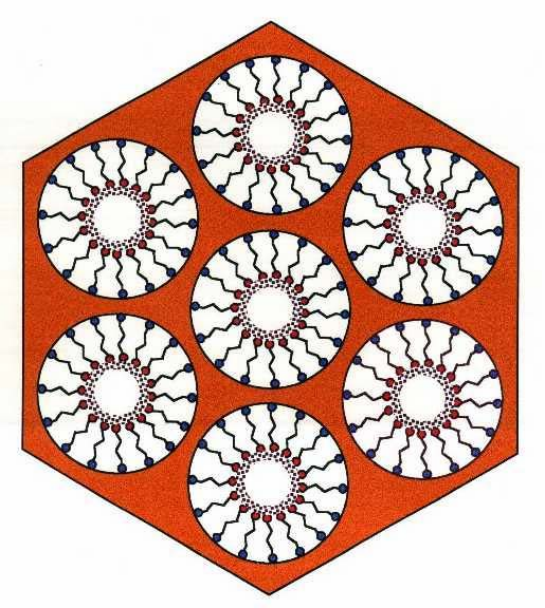
Templated Nanoporous Titania Thin Films

- Use well-established quaternary ammonium salt surfactant templating methodology to create nanostructured greenbody
- Extend methodology developed at PNNL to prepare nanoporous titania with well-defined pore structures and surface areas >300 m2/g
- Using biomimetic thin film deposition and/or spin-coating, prepare these nanoporous oxides in thin film format on a conducting oxide electrode interface



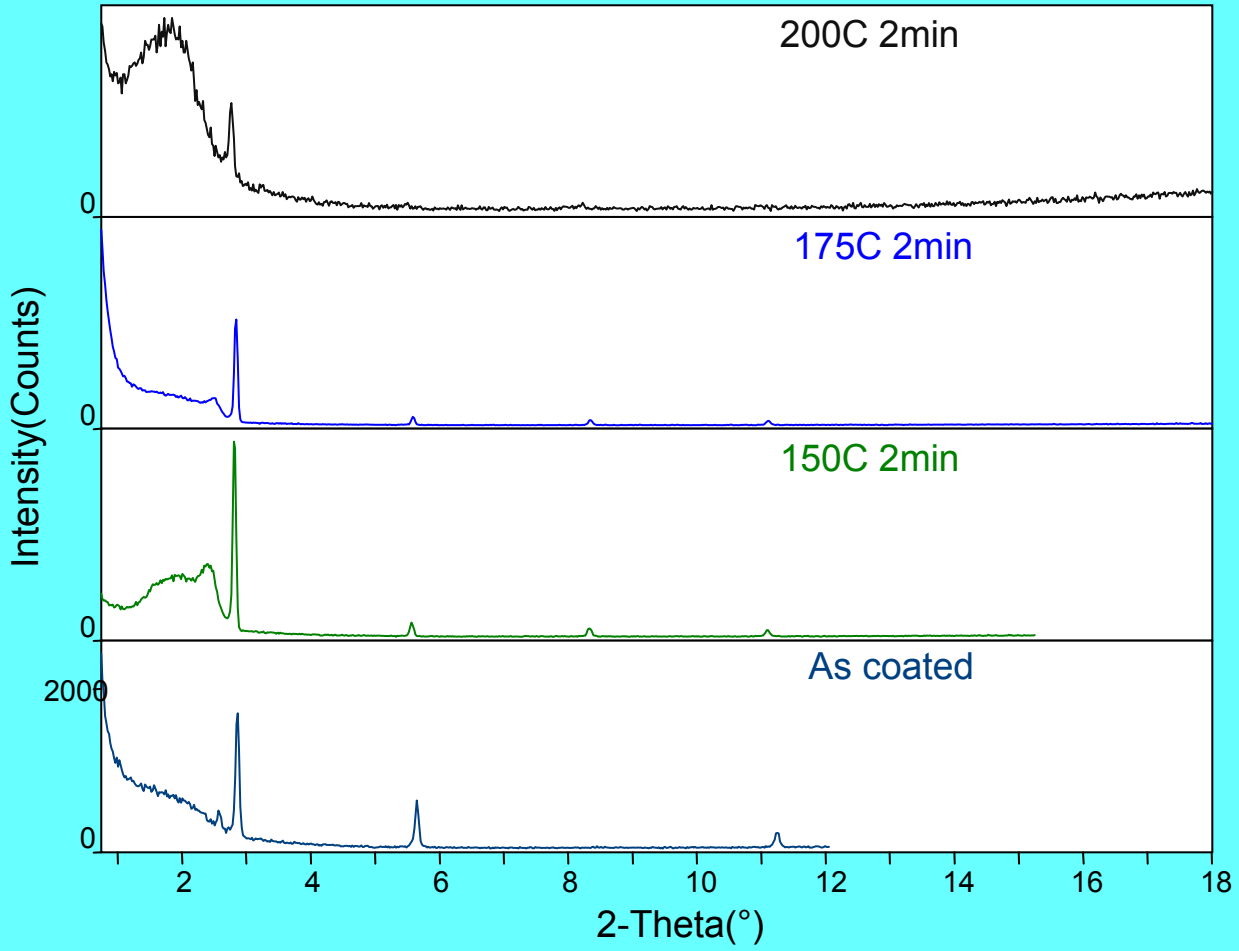
Prevention of Sintering

- Remove surfactant template at low temperatures using direct surfactant replacement (alternatives to calcination, e.g. extraction, displacement, plasma, etc.)
- Silane monolayer should form a kinetic barrier to structural collapse (similar to zirconia used previously)
- Continuous, open pore structure and high surface area maintained and allows for direct attachment of dye molecule



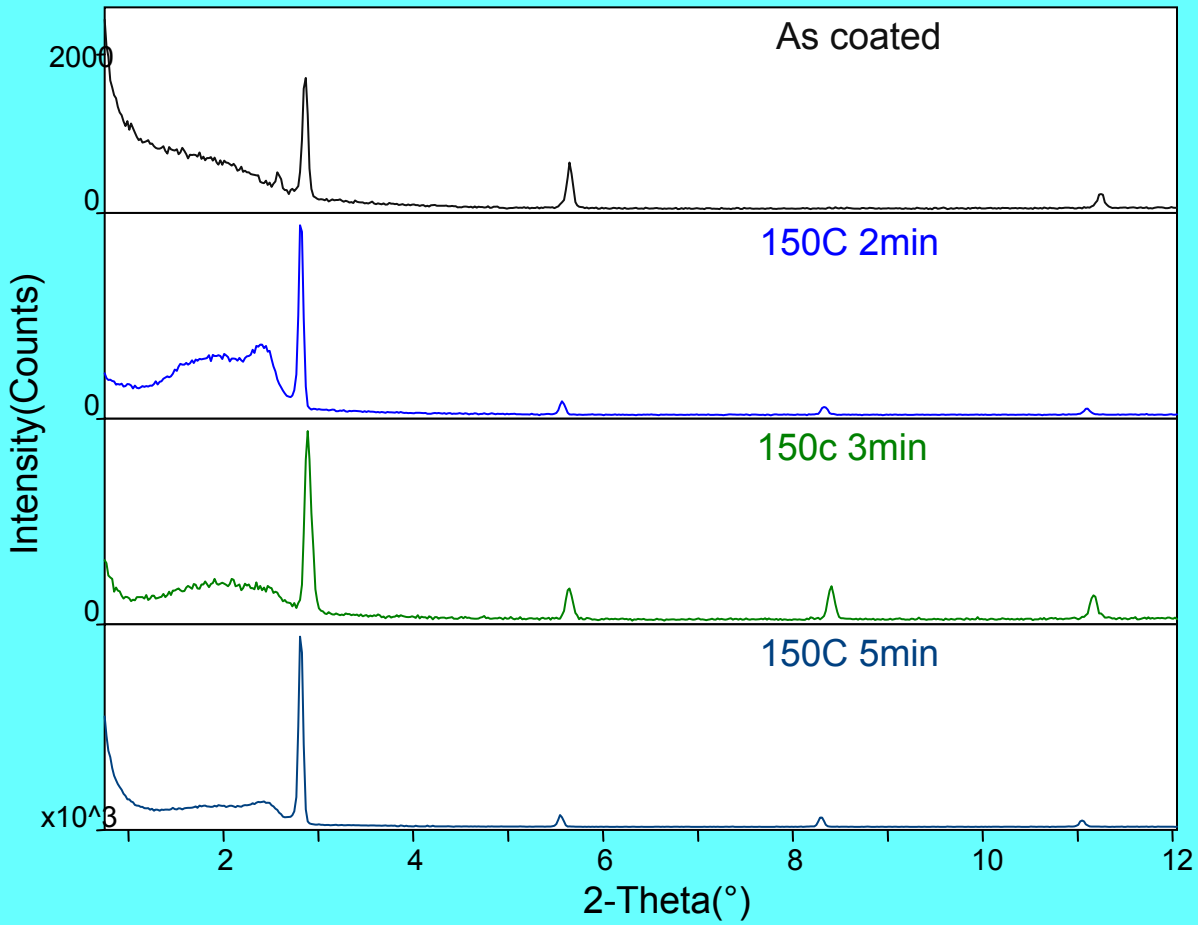
Thermal Curing of Mesoporous TiO2 Thin Films

The as-spun film is deposited in a lamellar structure. Heating the as-spun thin film induces structural reorganization, and ultimately, structural collapse.

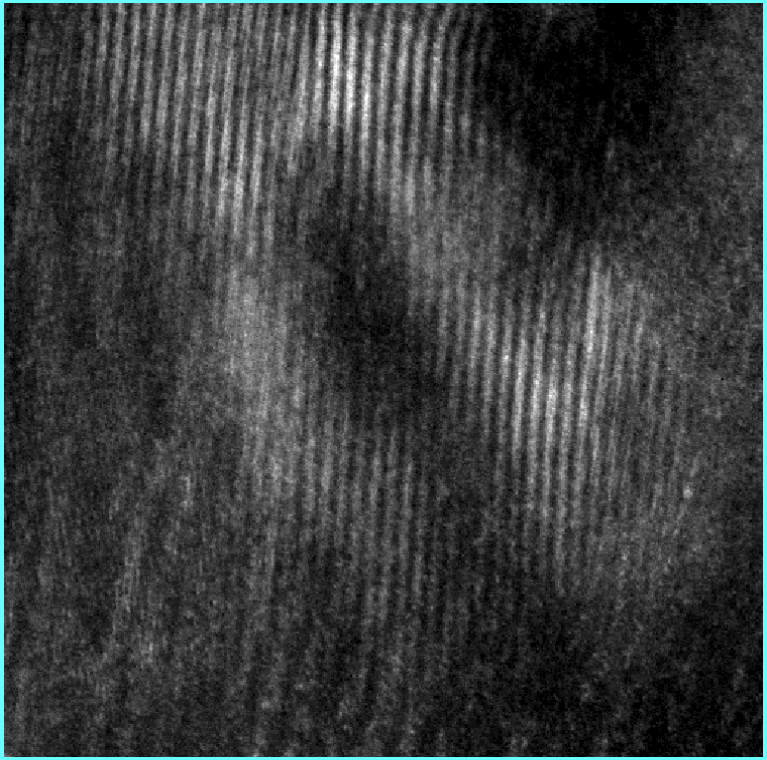


Kinetics of Thermal Curing

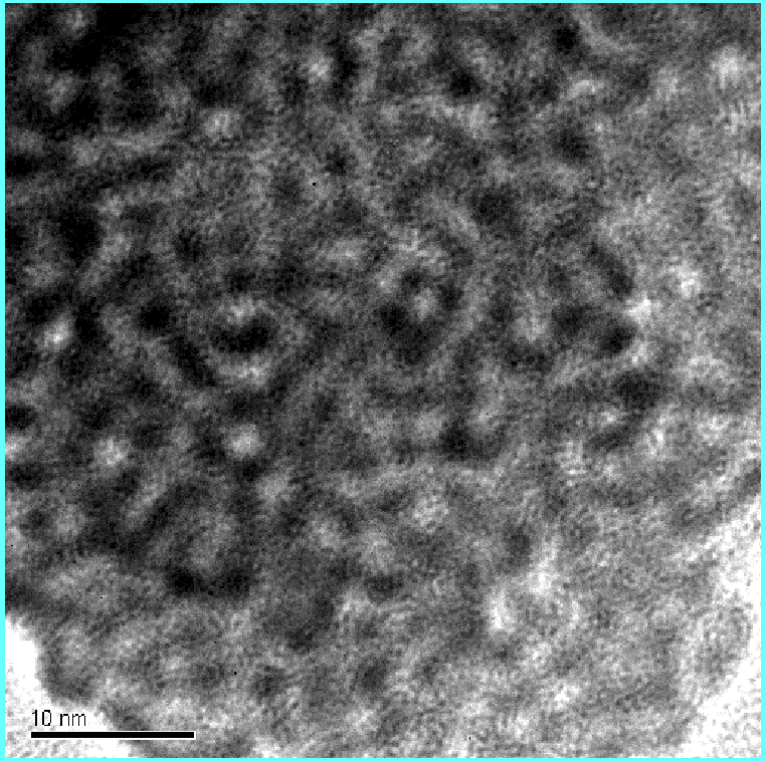
Thermal curing of the templated titania thin film appears to be virtually complete after 5 minutes at 150°C (higher temperatures were found to be deleterious).



Structure of Templated TiO_2 Thin Films



TEM of as-spun CTAC film



TEM of heat-treated CTAC film

Titania Nanorods

- A porous, permeable thin film can also be generated via templated nanorod morphology
- Offers a calcined (densified) titania structural component (possibly a better conduction path)
- Same monolayer chemistry can be utilized to decorate nanorod interface with dye molecules

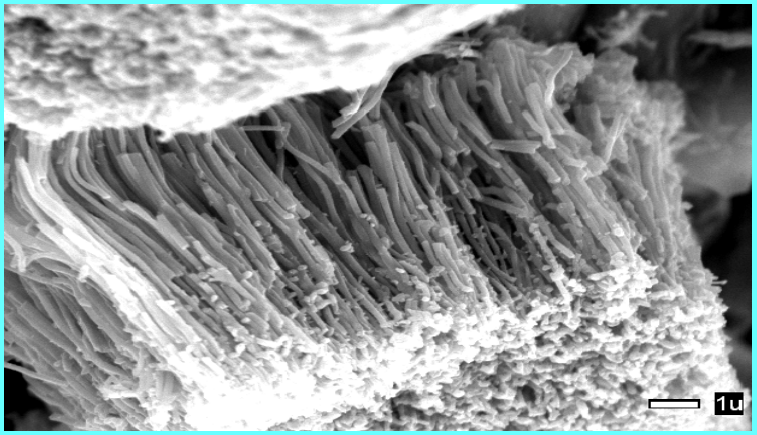


Figure 1. SEM of dense TiO_2 nanorods.

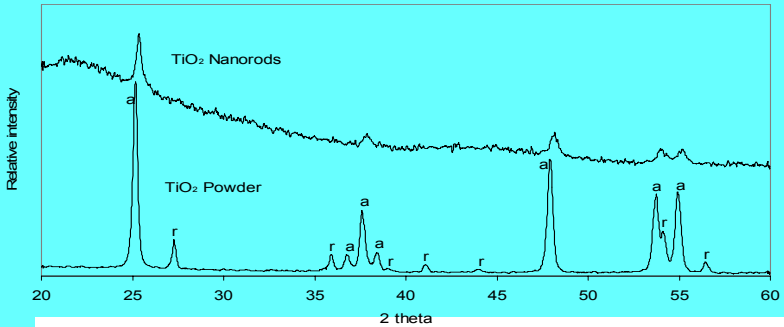


Figure 2. XRD of sol-gel-derived TiO_2 powder and nanorods.

Nanostructured Organic-Inorganic Semiconductor (NOIS) Electrodes

Functionalized Titania Nanorod Films

- Titania nanorods will be grown on conducting oxide foundation and coated using the same monolayer chemistry as the mesoporous titania thin films
- Electrophoretic deposition can also be used to grow mesoporous titania nanorods, offering higher surface area and greater dye incorporation

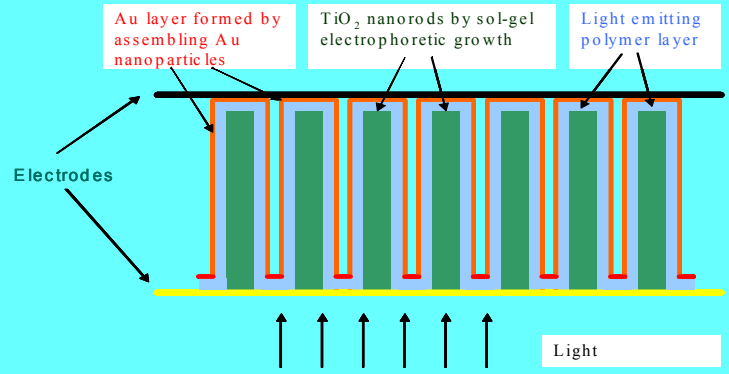


Figure 3. Schematic of proposed dye-sensitized TiO_2 solar cell system.

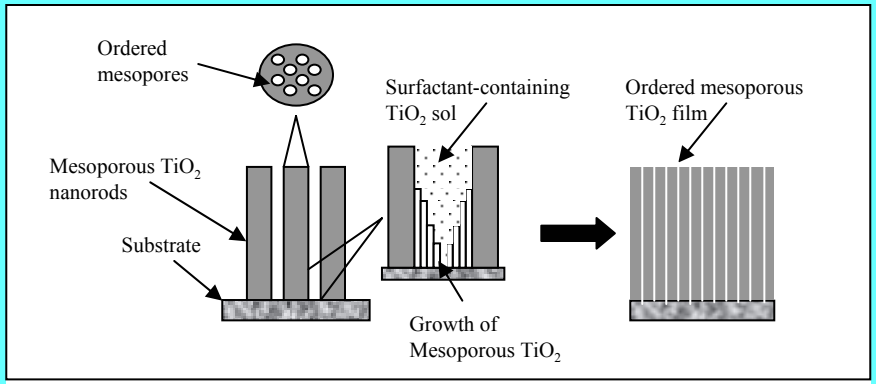
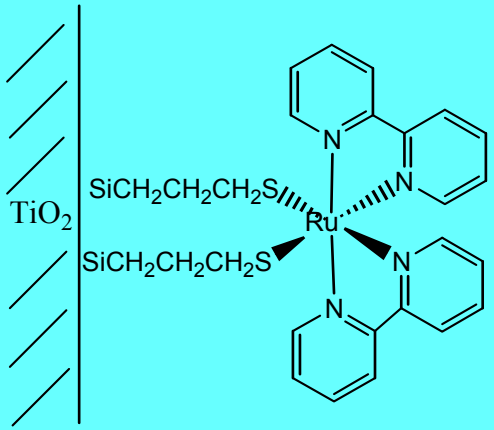


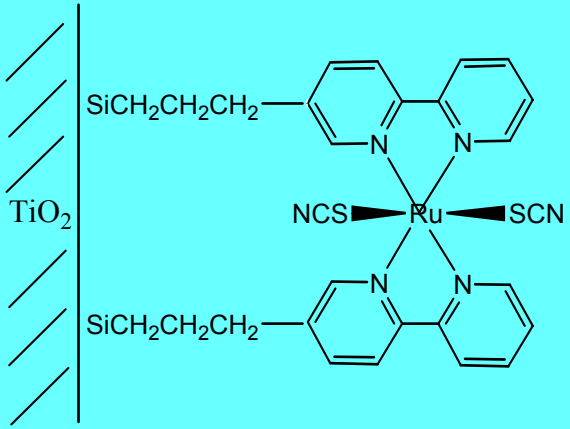
Figure 4. Schematic of ordered mesoporous TiO_2 film formation. The formation of mesoporous TiO_2 nanorods initiates the formation of mesoporous TiO_2 film with pores unidirectionally aligned perpendicular to the substrate after immersion in surfactant-containing TiO_2 sol.

Nanostructured Organic-Inorganic Semiconductor (NOIS) Electrodes

Self-Assembled Monolayer Chemistry

- Apply PNNL experience in deposition of functionalized fully dense self-assembled monolayers to insure maximal loading of dye molecules along pore interfaces
- Approach allows for ready control of the electronic factors involved in photon absorption, such as excited state energy, excited state lifetime, ionization potential, and possible decay mechanisms
- In addition, this strategy allows for control of the physical parameters associated with the dye/semiconductor distance, pore diameter, etc.





Interfacial Architecture

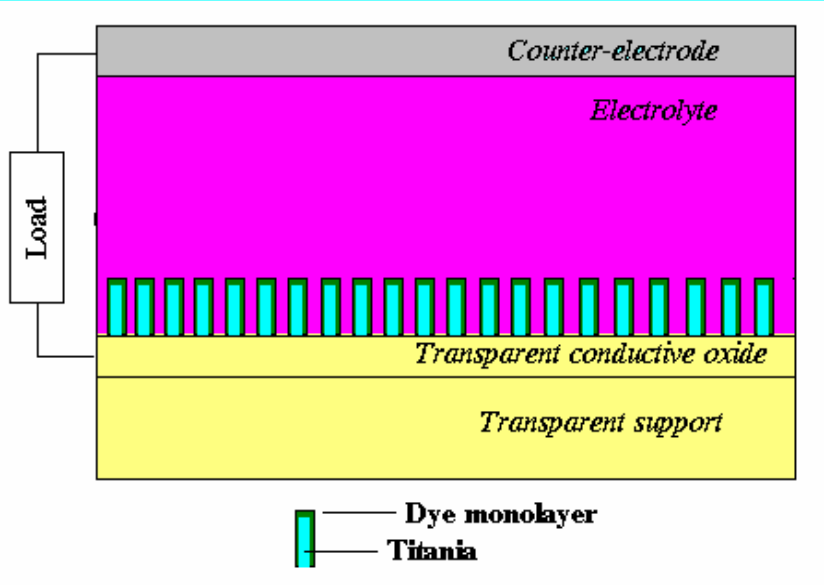
Improvements

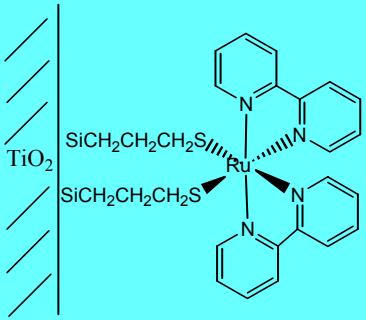
Shorter diffusion path = faster response time

Open pore structure = faster diffusion

Higher surface area = higher dye concentration

Monolayer chemistry inhibits back electron transfer

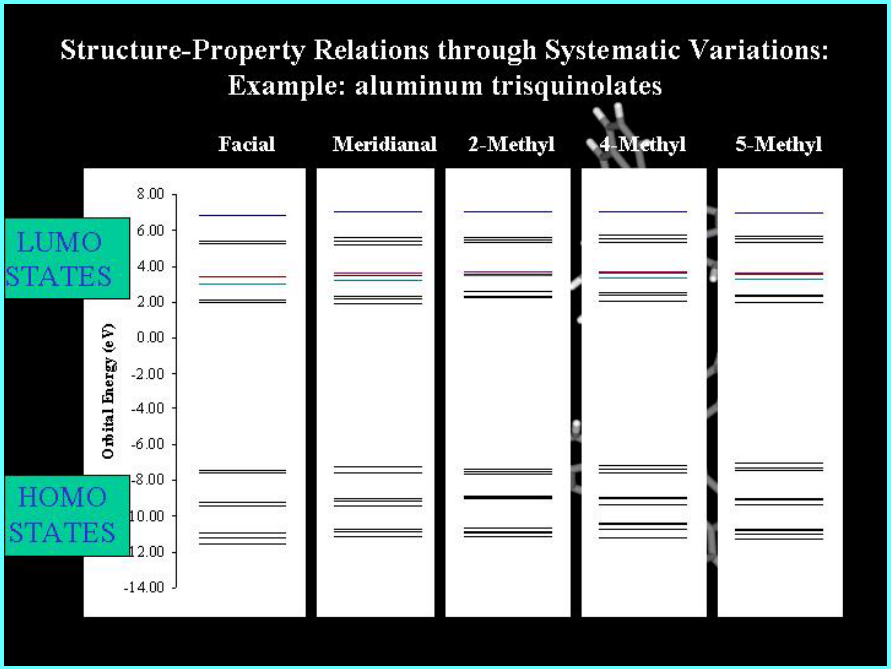




This research joins several disciplines: templated nanostructured ceramic synthesis, molecular self-assembly, organometallic photochemical electron transfer, catalysis, photovoltaics.

Modelling Charge Injection

- Evaluate charge injection efficiency, electron transfer rate across interfacial barrier layer, back electron transfer rate, effect of pore structure/wall thickness/dye density on charge injection efficiency, effect of pore diameter/structure on cell response time (electrolyte diffusion kinetics)
- What effect does the insulating interlayer have on back electron transfer?
- Can we design a system suitable for hole injection and what chemical composition will be required?



Example work in progress:
Ab-initio and semi-empirical modelling of metal chelates

Summary of results to date

- Successfully made mesoporous titania thin films (0.2 to 1 micron)
- Initial morphology is lamellar for both CTAC and non-ionic surfactants
- Lamellar phase rearranges to worm-hole structure on prolonged standing (1-2 weeks), can be accelerated thermally
- Nanostructure collapses upon calcination
- Monolayer studies underway
- Photoconductivity studies initiated