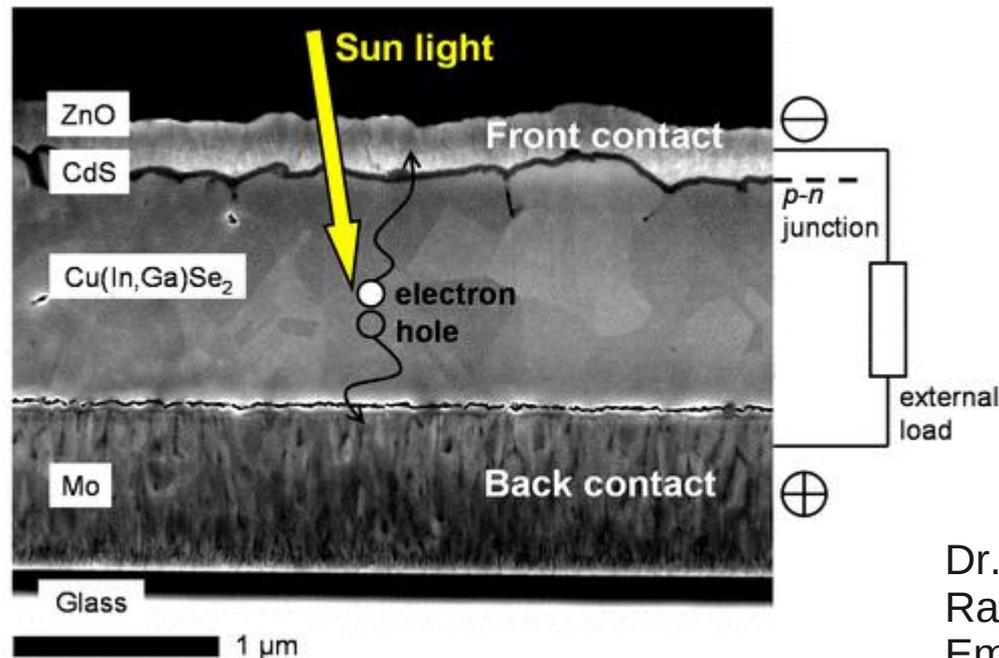
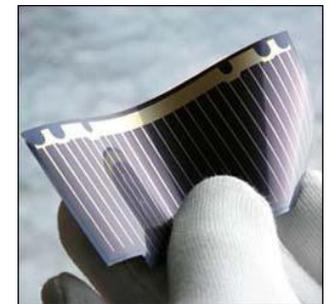
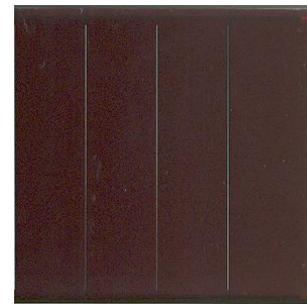
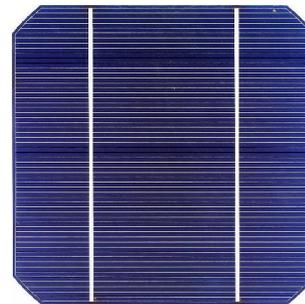
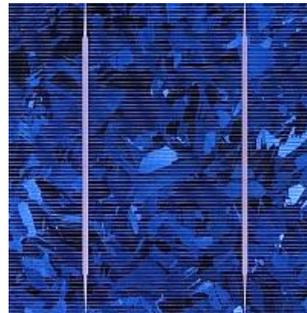


## Dye Sensitized Solar Cells (27027-01)

(Dienstag, 8:00-10:00 Departement Physik, Seminarzimmer 3.12)



Dr. Thilo Glatzel  
 Raum 3.04  
 Email: [thilo.glatzel@unibas.ch](mailto:thilo.glatzel@unibas.ch)

## Übersicht der Vorlesung

<b>22.02.2011</b>	allg. Einführung in die Solarenergie
<b>01.03.2011</b>	Physikalische Grundlagen der Photovoltaik I
<b>08.03.2011</b>	Physikalische Grundlagen der Photovoltaik II
<b>15.03.2011</b>	(Fastnachtsferien)
<b>22.03.2011</b>	Photochemische und photoelektrische Methoden der Energiewandlung
<b>29.03.2011</b>	Aufbau der Farbstoffsolarzelle, vgl. org. Solarzelle
<b>05.04.2011</b>	TiO <sub>2</sub> Nanopartikel als Substrat der Farbstoffsolarzelle
<b>12.04.2011</b>	Geeignete molekulare Farbstoffe zur Sensibilisierung
<b>19.04.2011</b>	Funktionsweise und Alternativen für den Elektrolyten
<b>26.04.2011</b>	(Osterferien)
<b>03.05.2011</b>	(FANAS meeting)
<b>10.05.2011</b>	Solid-State Dye-Sensitized Solar Cells
<b>17.05.2011</b>	Experimentelle Methoden zur Solarzellen-Charakterisierung
<b>24.05.2011</b>	Bau und Charakterisierung eigener Solarzellen
<b>31.05.2011</b>	



## Funktionsweise und Alternativen für den Elektrolyten

### Solid-State Hole Conductors

#### **Solid-State Hole Conductors**

- spiro-OMeTAD
- Influences of Additives
- Charge Generation
- Reductive Quenching
- TiO<sub>2</sub> Pore Filling
- Recombination
- Block Copolymers

## Seminars

Marcus Wyss

*J. Phys. Chem. B* 2005, 109, 14945–14953

14945

### Electrochemical Impedance Spectroscopic Analysis of Dye-Sensitized Solar Cells

Qing Wang, Jacques-E. Moser, and Michael Grätzel\*

*Laboratory for Photonics and Interfaces, Institute of Chemical Sciences and Engineering, Ecole Polytechnique Fédérale de Lausanne, 1015 Lausanne, Switzerland*

*Received: May 25, 2005*

Nicolas Devantay



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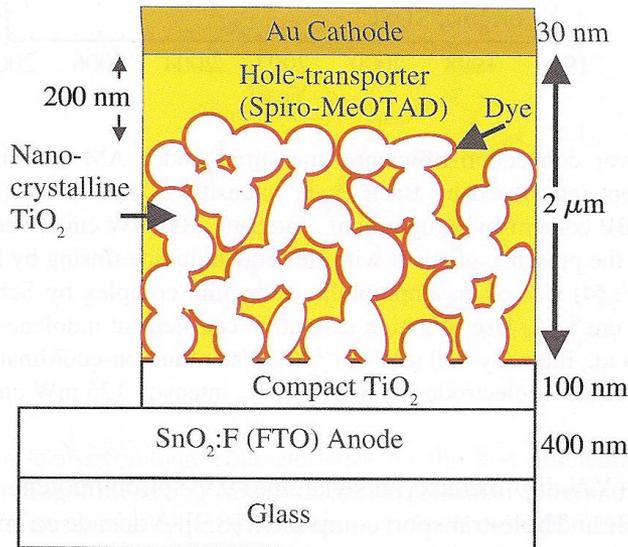


Analysis and simulation of incident photon to current efficiency in dye sensitized solar cells

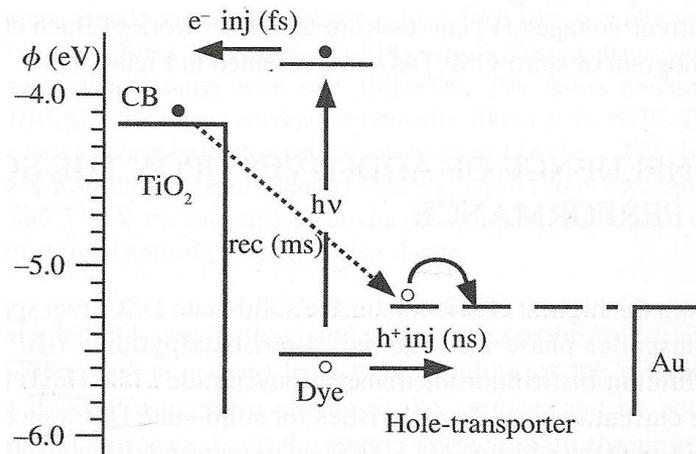
D. Gentilini\*, D. D'Ercole, A. Gagliardi, A. Brunetti, A. Reale, T. Brown, A. Di Carlo

*Centre for Hybrid and Organic Solar Energy, University Tor Vergata, Via del Politecnico 1, 00133 Rome, Italy*

## Solid-State Hole Conductors



(a)

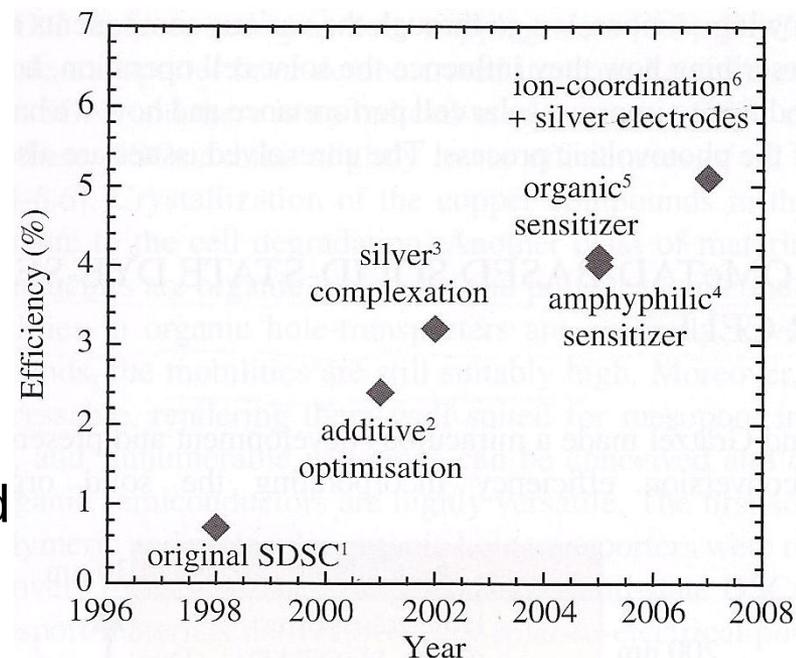
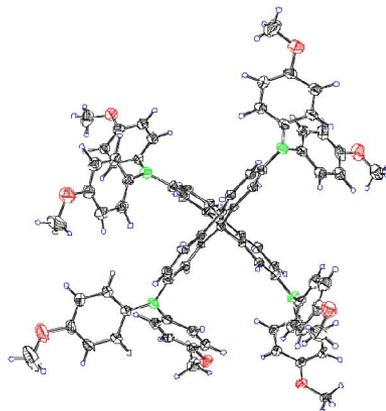


(b)

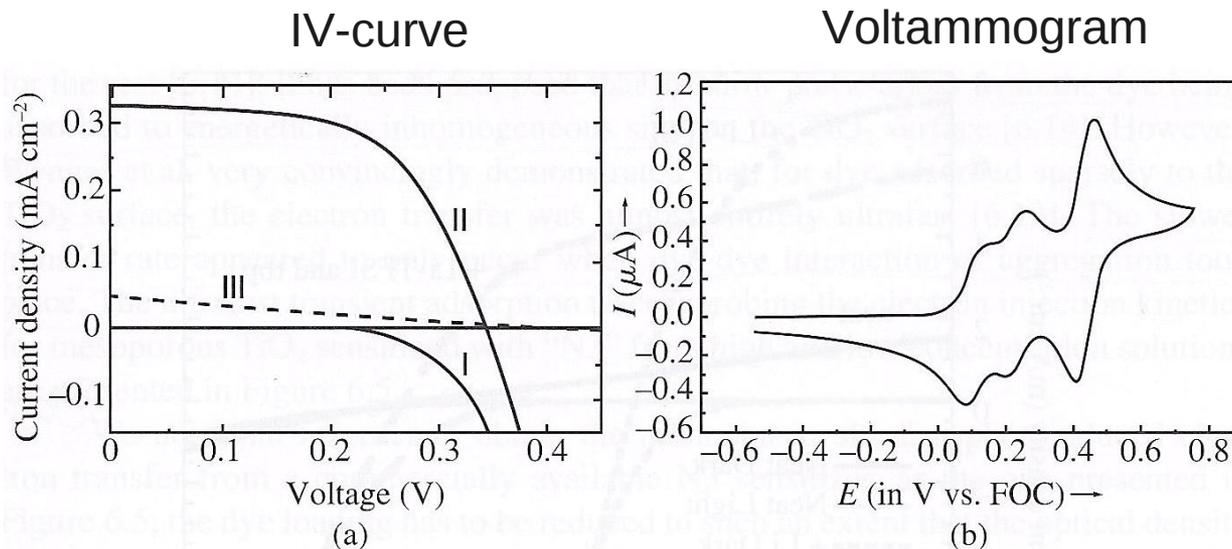
- Industry prefers to remove the liquid phase of the DSSC and realize an efficient all solid-state device (c.p. short life time and leakage issue with disposable batteries..)
- Gel and solid-state electrolytes might still be corrosive
- Requirements: deposition and fully interpenetrate the nanoporous  $\text{TiO}_2$
- Inorganic CuI showed 4.7%, but cells are unstable, CuSCN better

## Solid-State Hole Conductors

- Polymeric and molecular organic hole transporters
  - Charge mobility lower
  - Molecules are solution processable
  - Cheap
  - Easy to vary
- Spiro-OMeTAD
  - Methoxy triaryl diamine substituted spiro centered



## spiro-OMeTAD



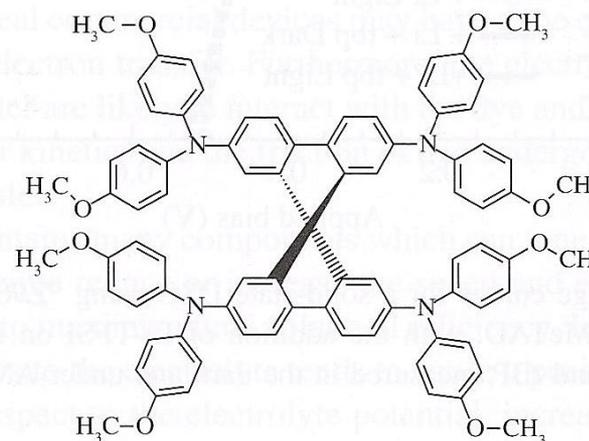
Additives:

$N(\text{PhBr})_3\text{SbCl}_6$  0.33mM

$\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$  15mM

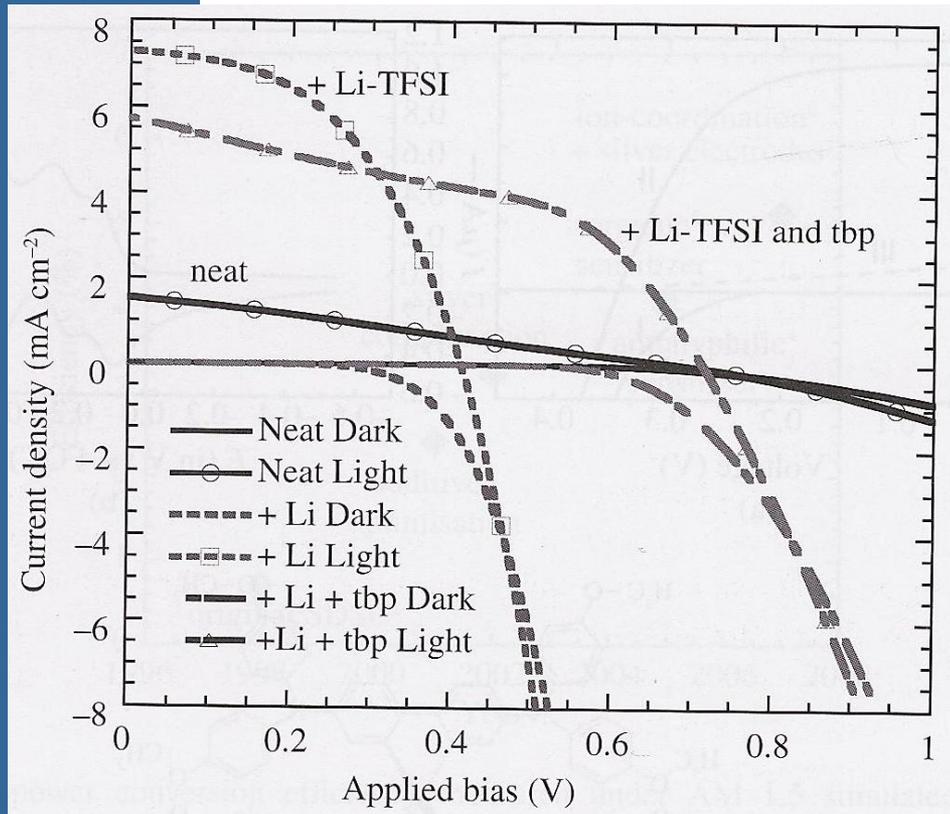
In chlorobenzene

With 5% acetonitrile



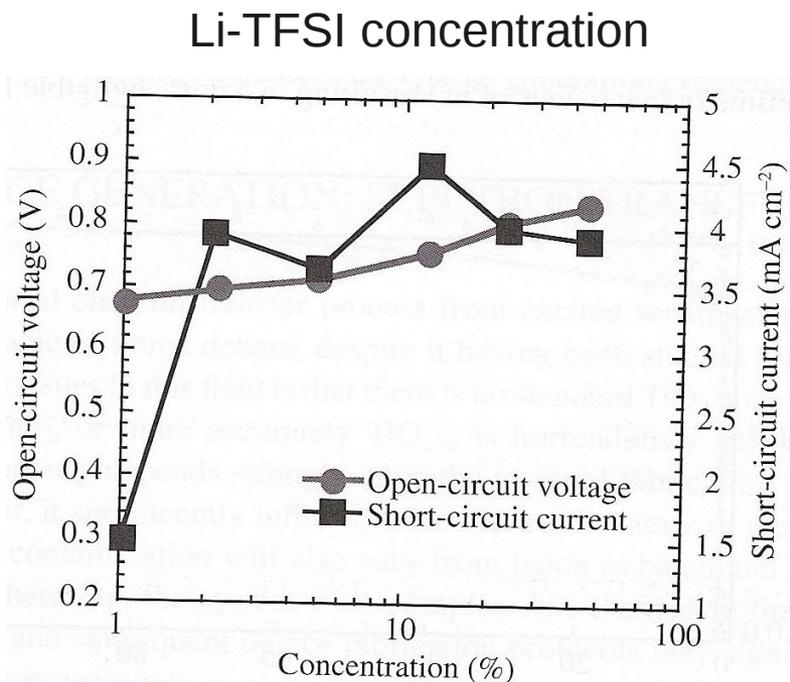
(c)

## Influences of Additives



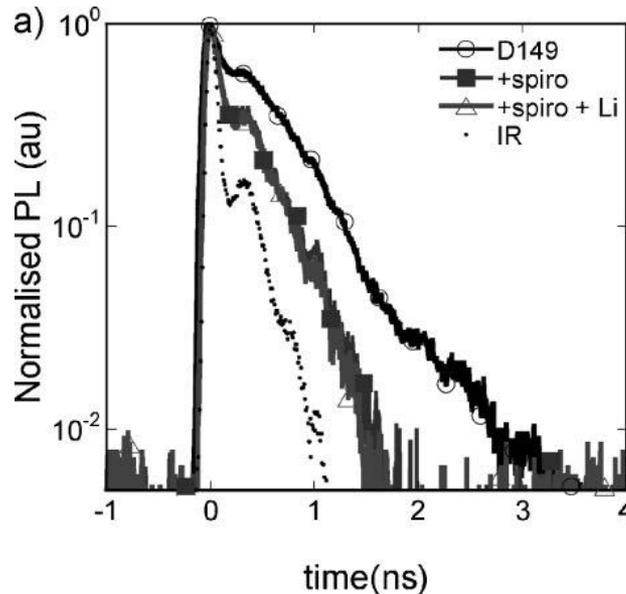
- **4-tert-butylpyridine (tBP)**
  - Helps to solve the salt (inhibiting it from absorbing to the surface)
  - Positive shift of the  $\text{TiO}_2$  CB (weak binding of the pyridine to  $\text{TiO}_2$  which donates an electron to the surface (positive charge repels holes from  $\text{TiO}_2$ ))
- **Ionic salt (Li-TFSI) lithium-bis(trifluoromethanesulfonyl)imide**
  - Function not clear
  - Inhibits charge recombination
  - Increases charge carrier mobility
  - Maybe enhances charge generation efficiency

## Charge Generation: Electron Transfer

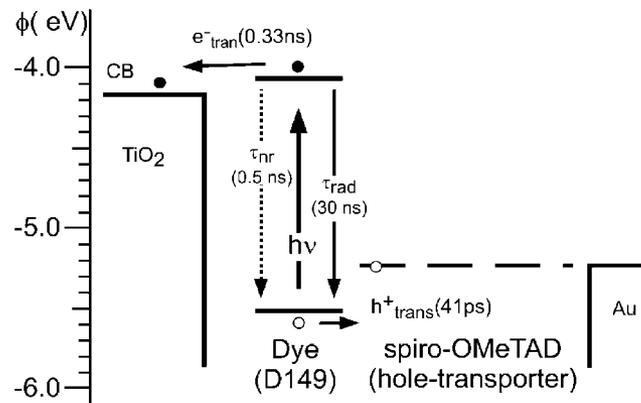


- TiO<sub>2</sub> variations (structural, electronic) strongly influencing the electron transfer
- Li-TFSI is influencing the  $I_{sc}$  and  $V_{oc}$  but stabilizes fast
- No positive shift of the CB from TiO<sub>2</sub>
- Coadsorption of dipolar molecules

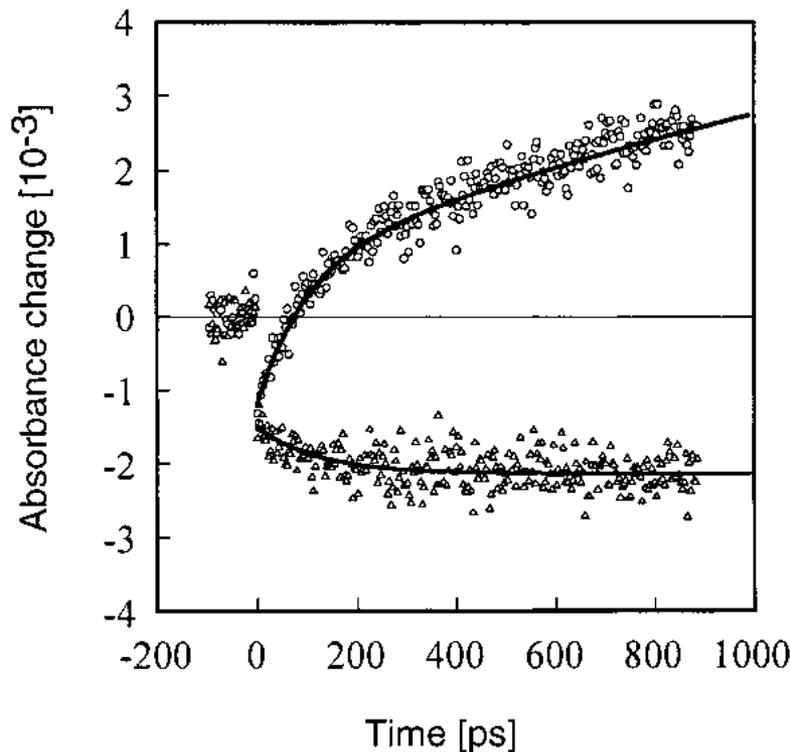
## Reductive Quenching



- Indoline-based organic sensitizer D149
- Reductive quenching might be the main charge generation mechanism
- Electron transfer in 300ps
- Hole transfer in 40ps
- No influence on Li-TFSI



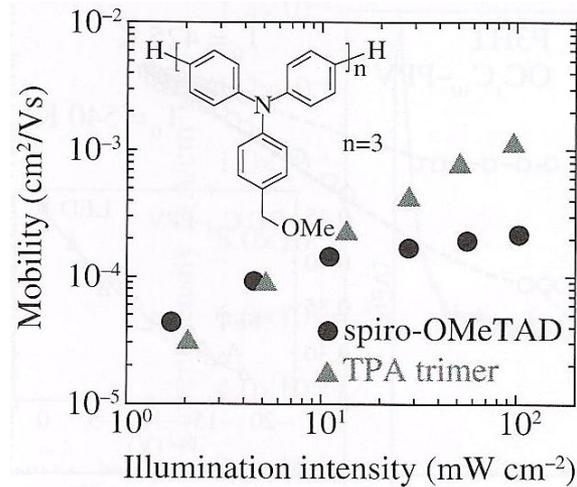
## Charge Generation: Hole Transfer



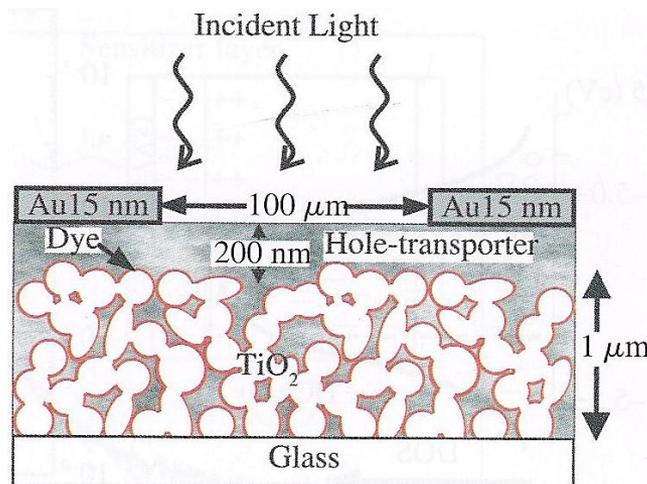
OMeTAD (○) and with PC/EC (▲)  
at 520nm after excitation at 602nm  
component lifetimes of 100 and 2300 ps

- N719 and spiro-OMeTAD
- Transient photoinduced absorption spectroscopy
- Sub-nanosecond dye regeneration
- Positive OMeTAD<sup>+</sup> cation radical absorption due to hole injection from the oxidized sensitizer into the hole conductor
- The wide time range over which the hole injection proceeds suggests that the dye is not perfectly contacted by the hole conductor

## P-doping: Conductivity and Hole Mobility

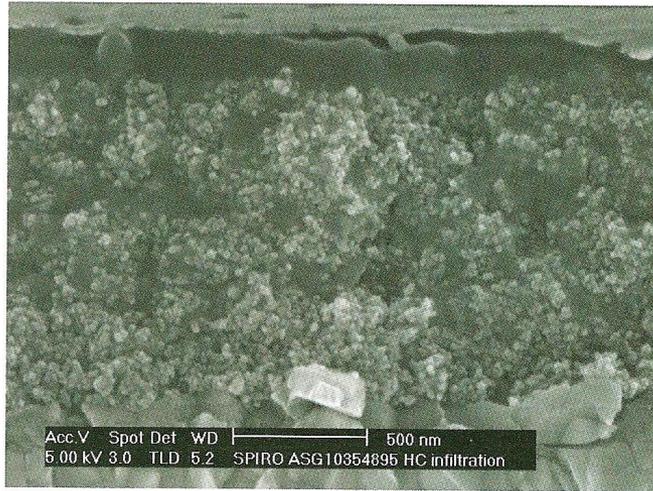


(a)

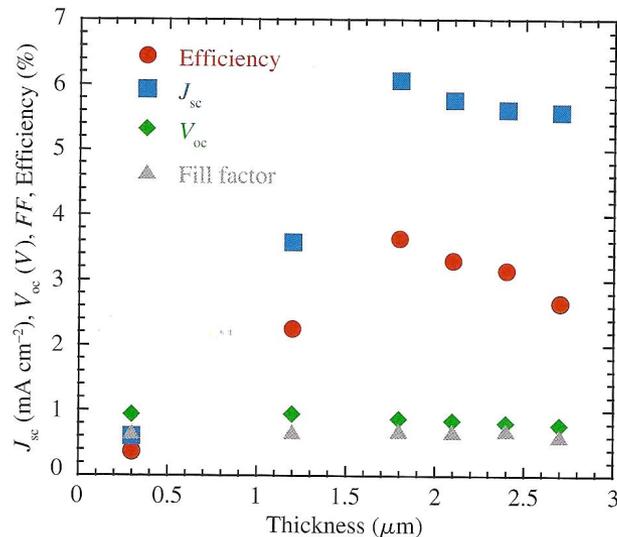


- Increased mobility due to p-doping
- Reduced serial resistance, improved FF
- Increasing recombination at TiO<sub>2</sub> interface
- Influenced film forming properties
- reduced mobility possible
- For spiro-OMeTAD negative influences outweigh advantages

## TiO<sub>2</sub> Pore Filling



(a)

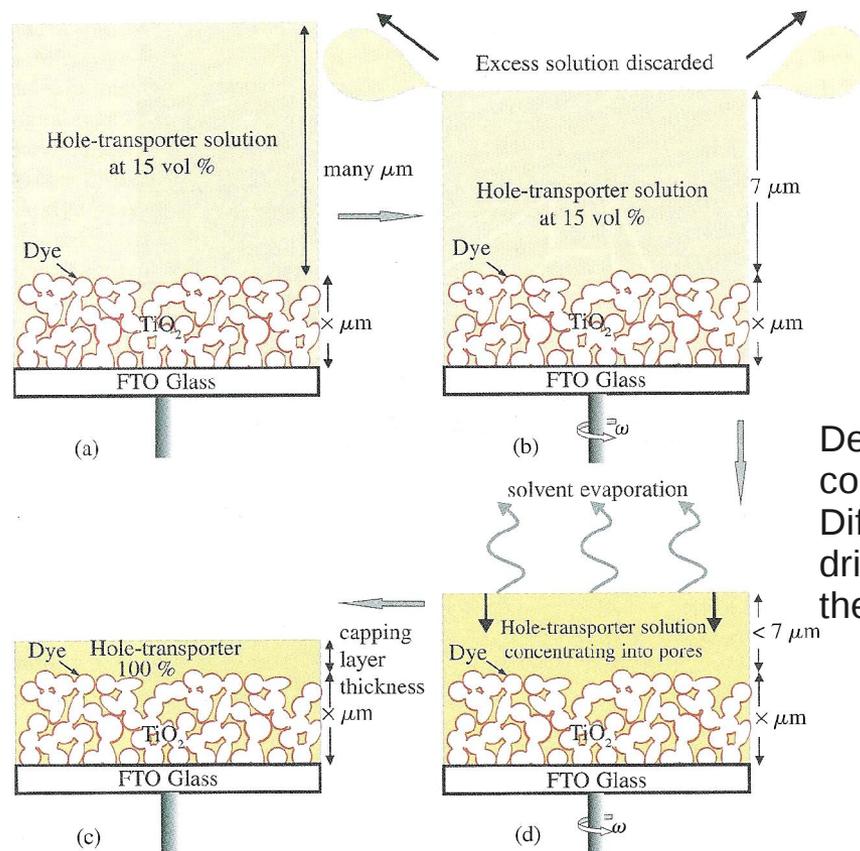


(b)

- Max efficiency at 2 μm thick TiO<sub>2</sub> films
- Diffusion length seems to be ok, so maybe pore filling a problem
- Test of more than thirty hole-transport materials with higher charge carrier mobility, but none shows higher efficiency

## Film Forming by Spin Coating

All pores are filled  
Excess of solution

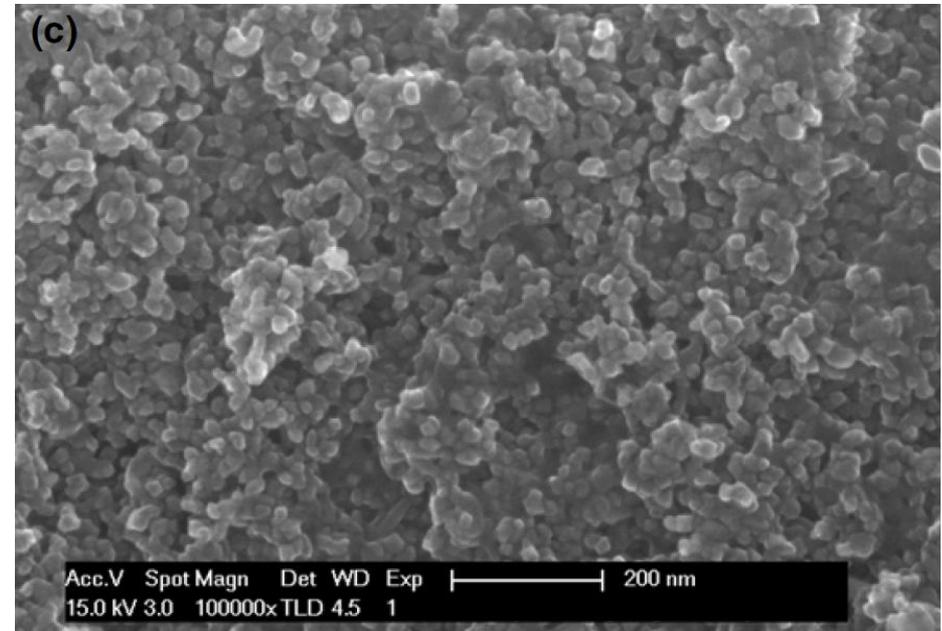
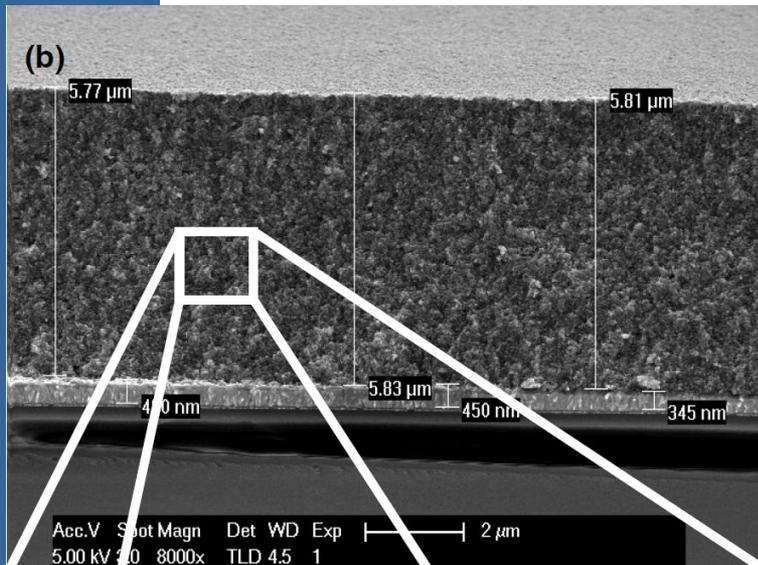
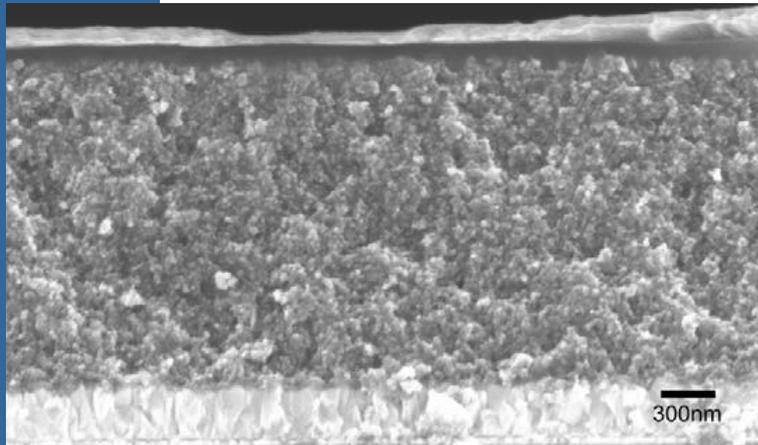


Film has uniform thickness  
Dependent on viscosity!

Development of a concentration gradient  
Diffusion and convection drives spiro-OMeTAD in the pores

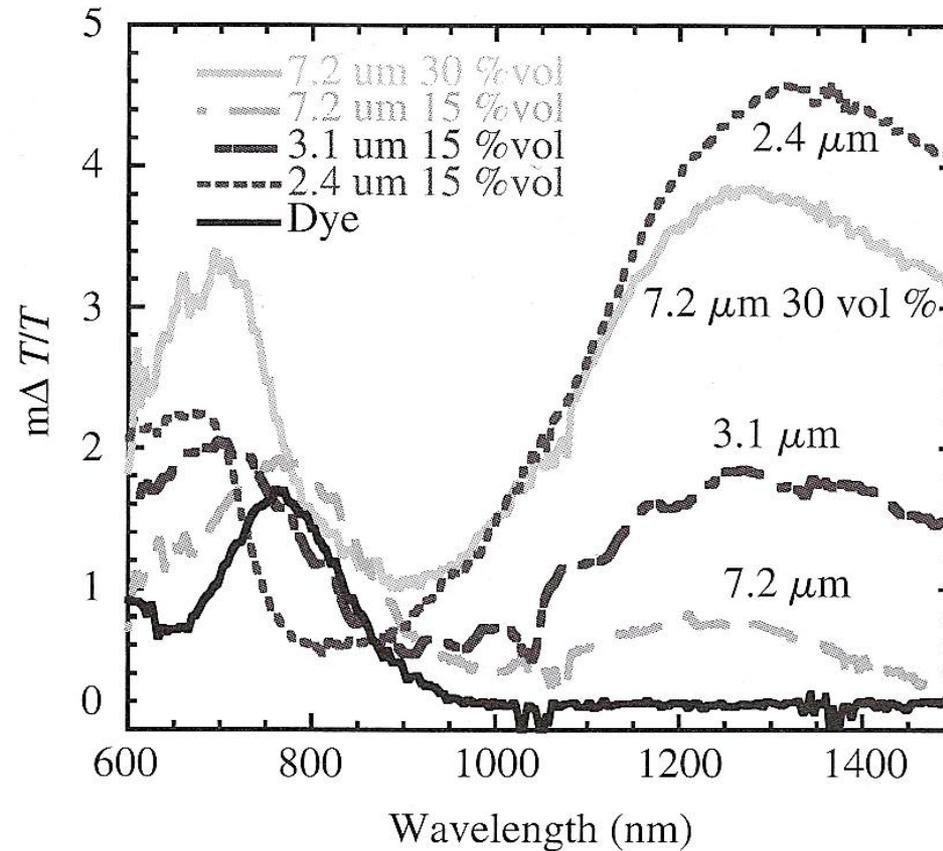
- Solvent typically chlorobenzene
- Not enough material to fill more than 2mm  $\text{TiO}_2$  with a porosity of 60%

## Film Forming by Spin Coating



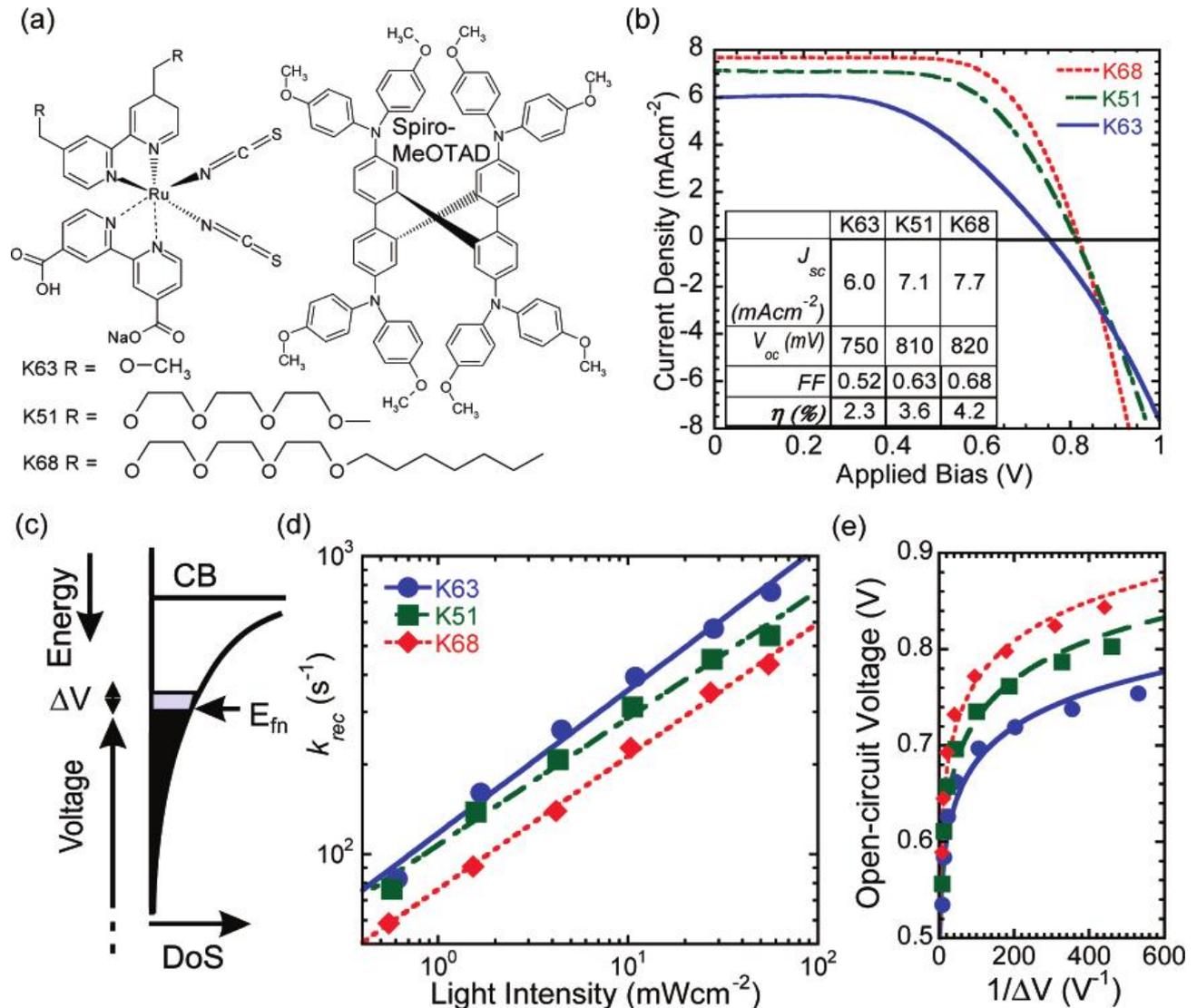
Not completely filled pores, no overlayer

## Photo Induced Absorption (PIA)

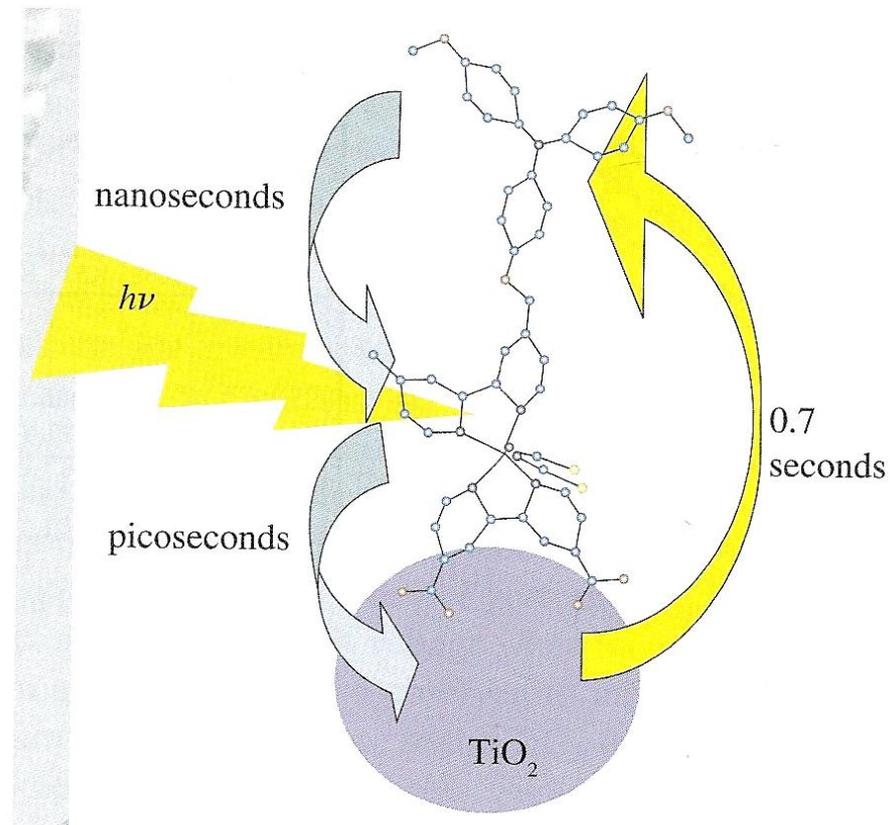


Measures degree of dye regeneration  
Oxidized dye signal at 800nm  
Spiro-OMeTAT at 700nm and 1.3 $\mu\text{m}$

## Recombination: Immobilize Lithium Ions



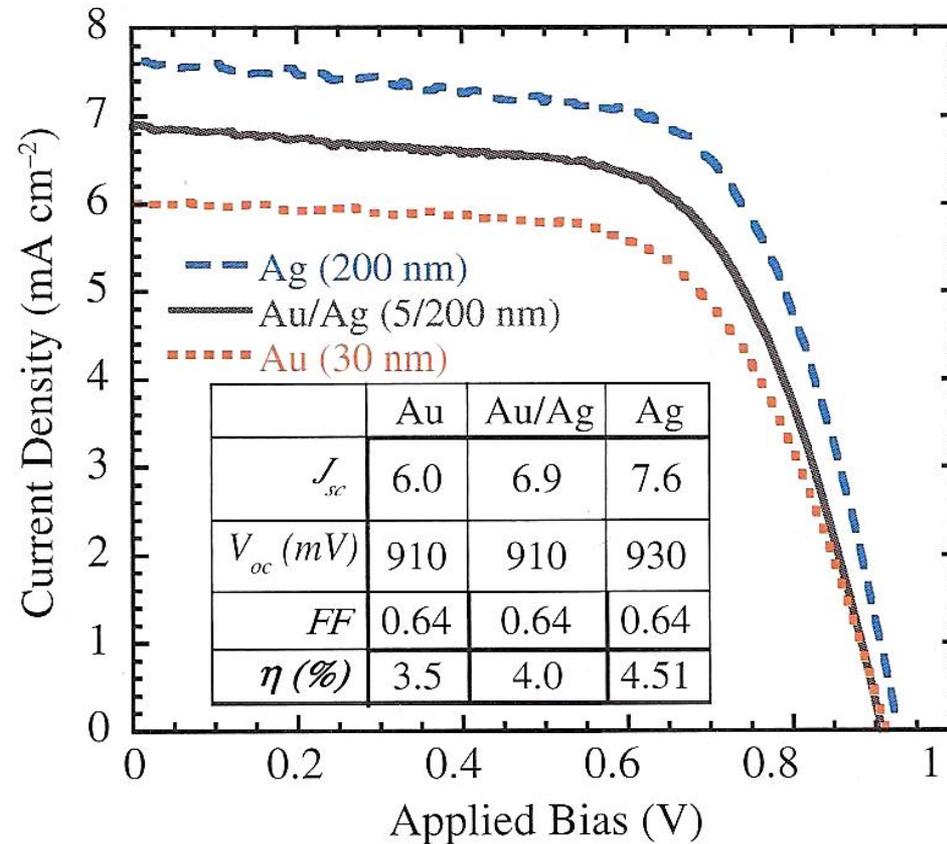
## Recombination: Spatial Recombination



Idea failed up to now.....

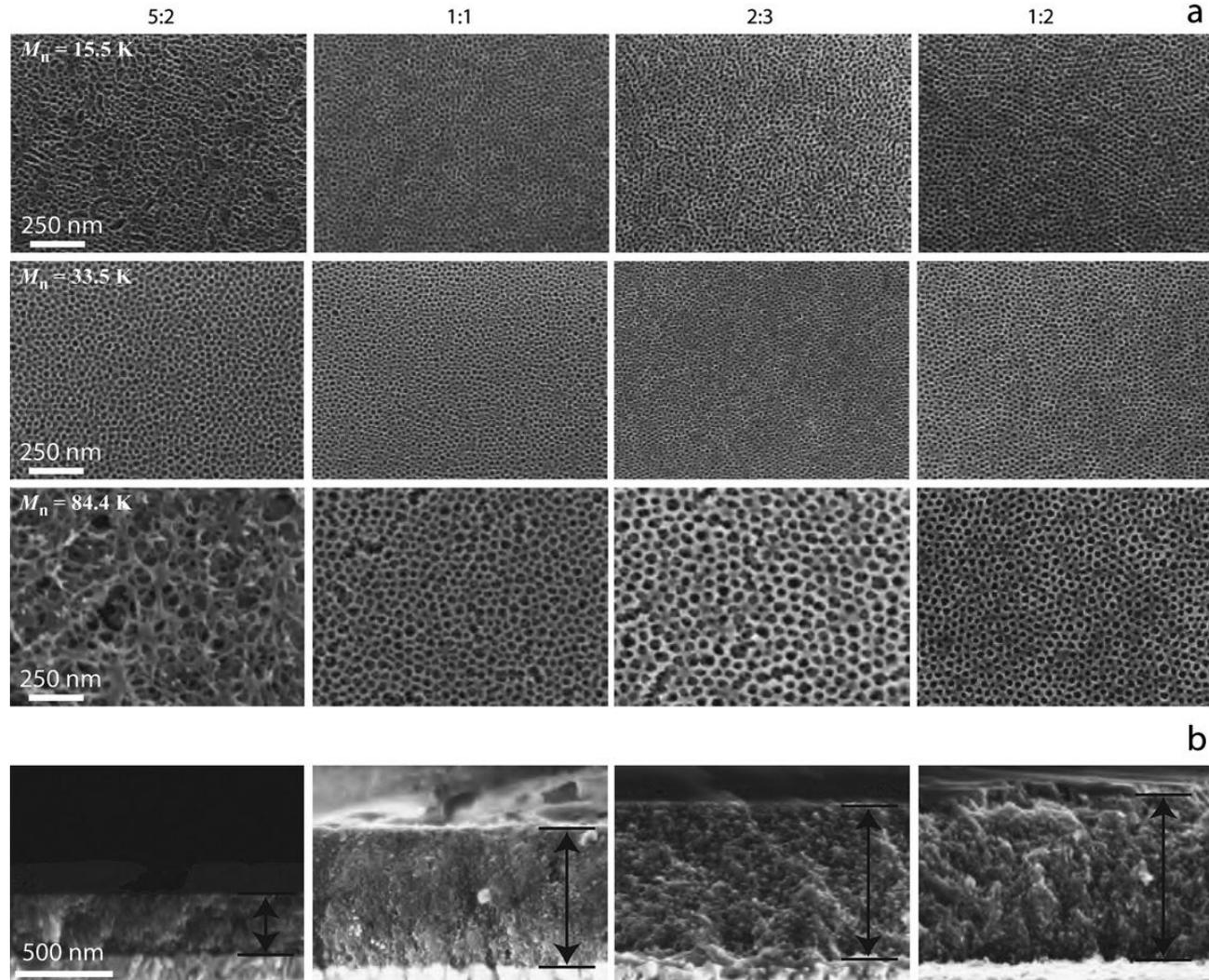


## Enhancing Light Capturing



Gold does not reflect light very well..... blue part is suppressed

## Alternative Structures: Block Copolymers



## Gyroid Network

