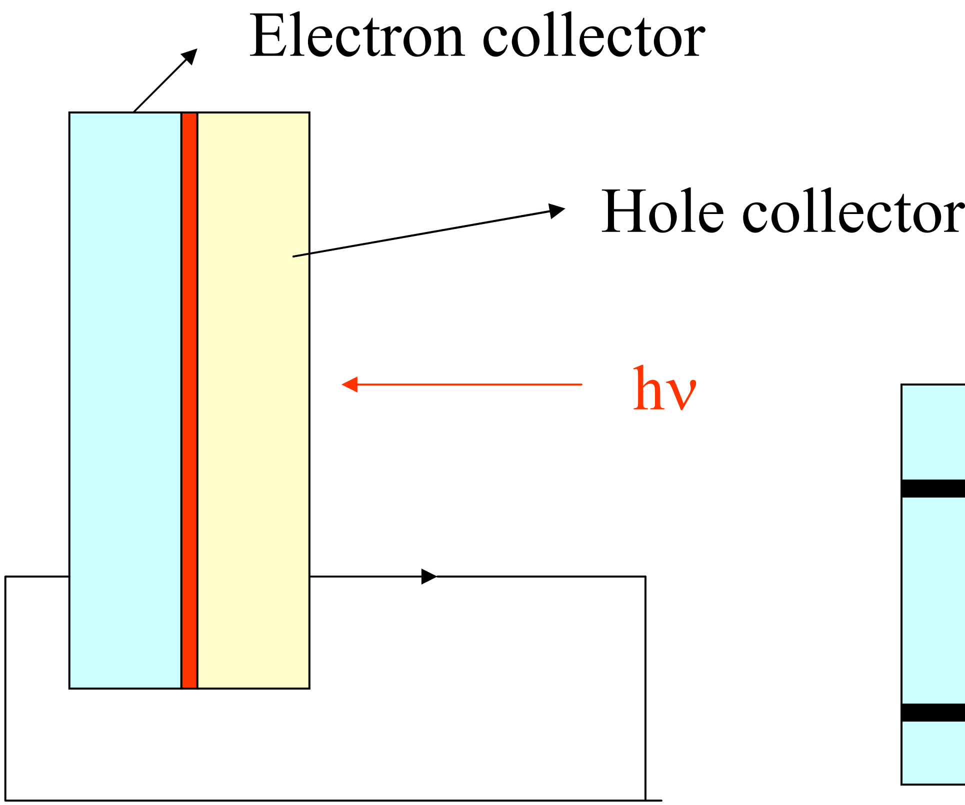
1/f Noise in Dye-sensitized Solar Cells and NIR Photon Detectors

P.K.D.D.P. Pitigala, M.K.I. Seneviratne ,
K.Tennakone
Institute of Fundamental Studies,Sri Lanka

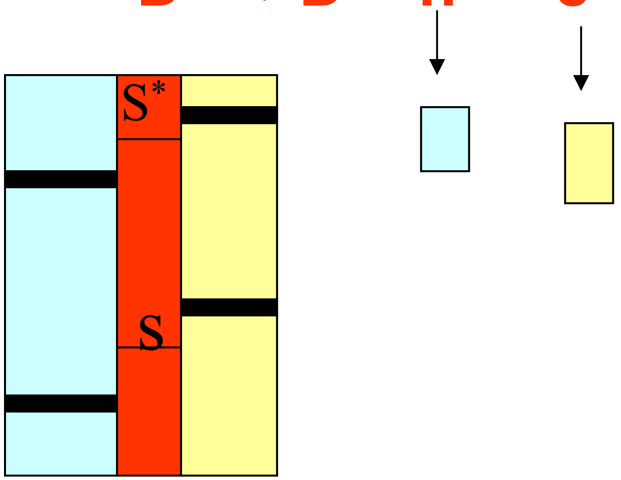
P.V.V Jayaweera ,A.G.U.Perera
Department of Physics and Astronomy,
Georgia State University, USA.

Dye-sensitized photon detector

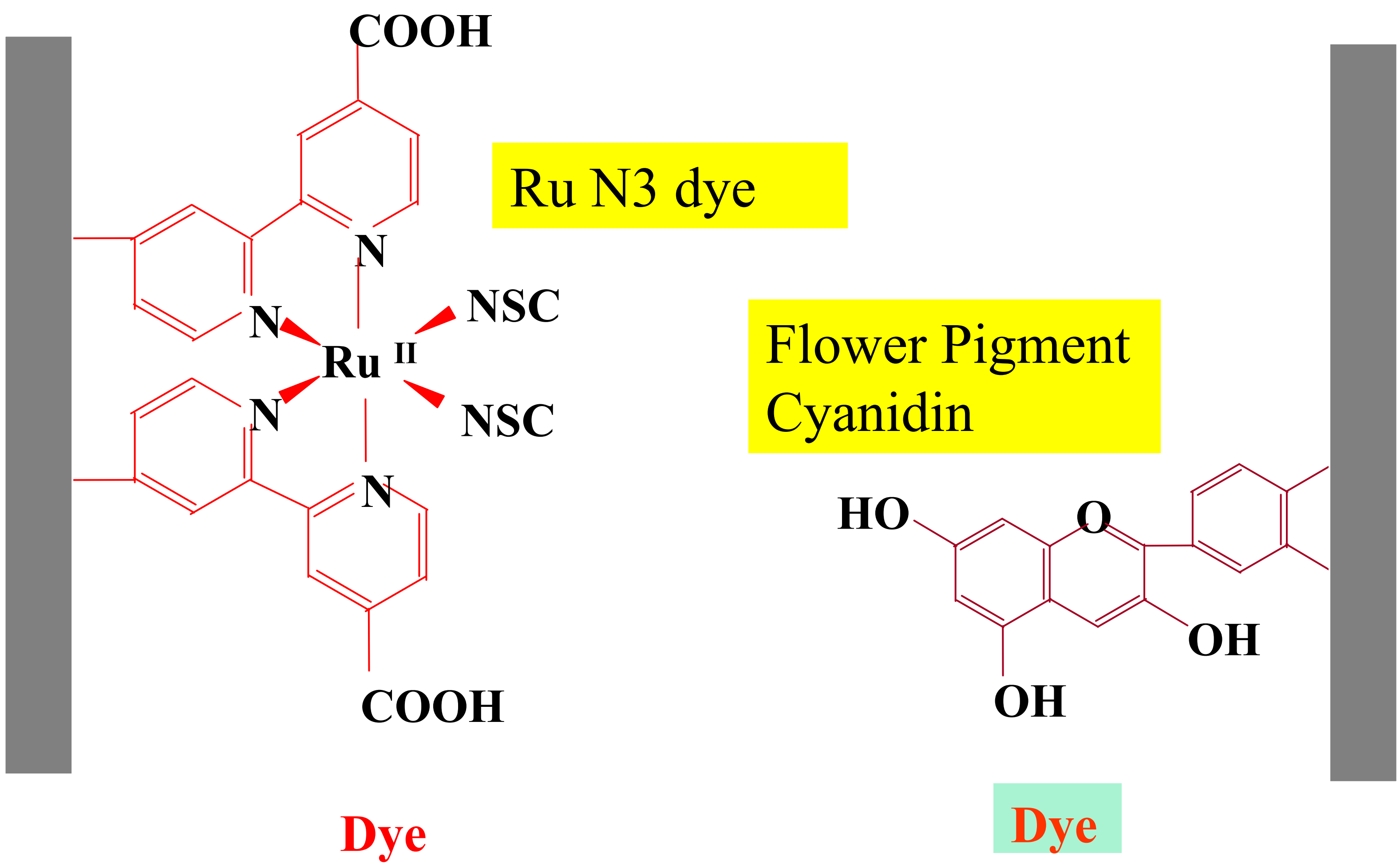


$$h\nu + D \rightarrow D^*$$

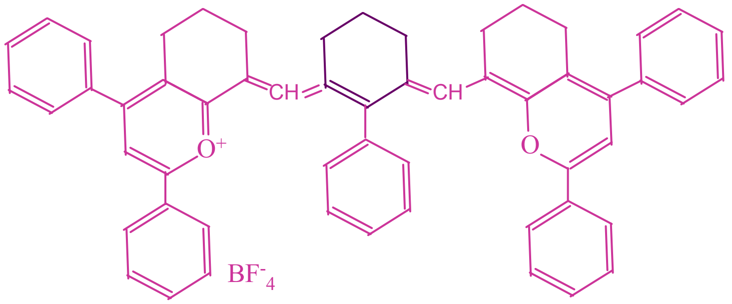
$$D^* \rightarrow D + h^+ + e^-$$



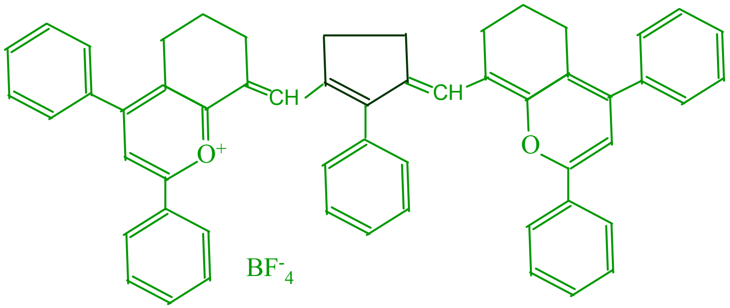
Bonding of Dyes to the TiO_2 Surface



IR DYES

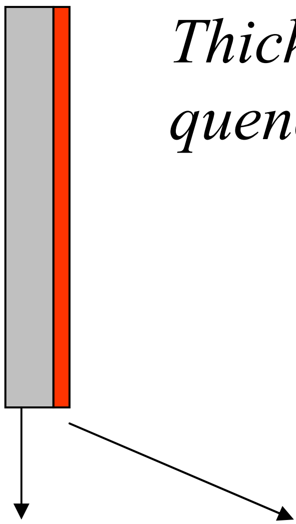


IR-1100



IR-1135

The problem of thick dye layers



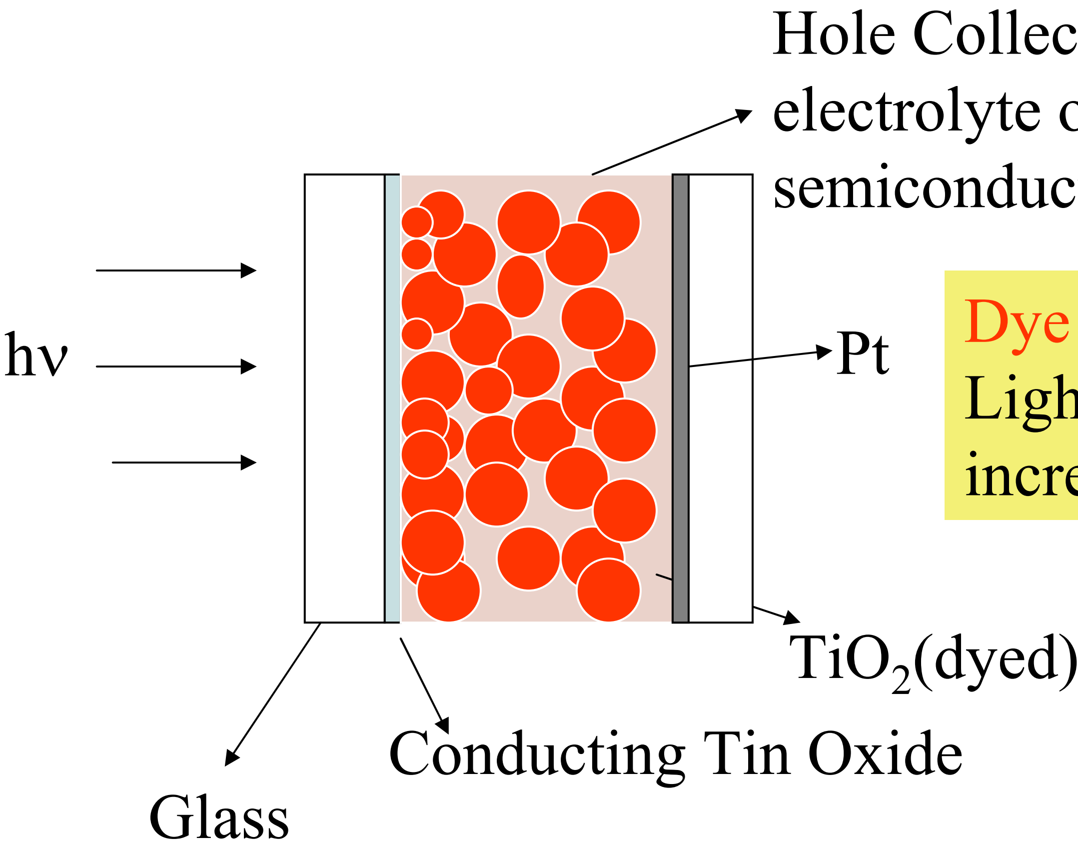
Thick dye layers are insulating and also causes quenching, i.e., $D^* + D^*$ --- $\rightarrow D + D + heat$

$D^* + D \text{ ---}\rightarrow D + D + heat$

Semiconductor Dye Monolayer

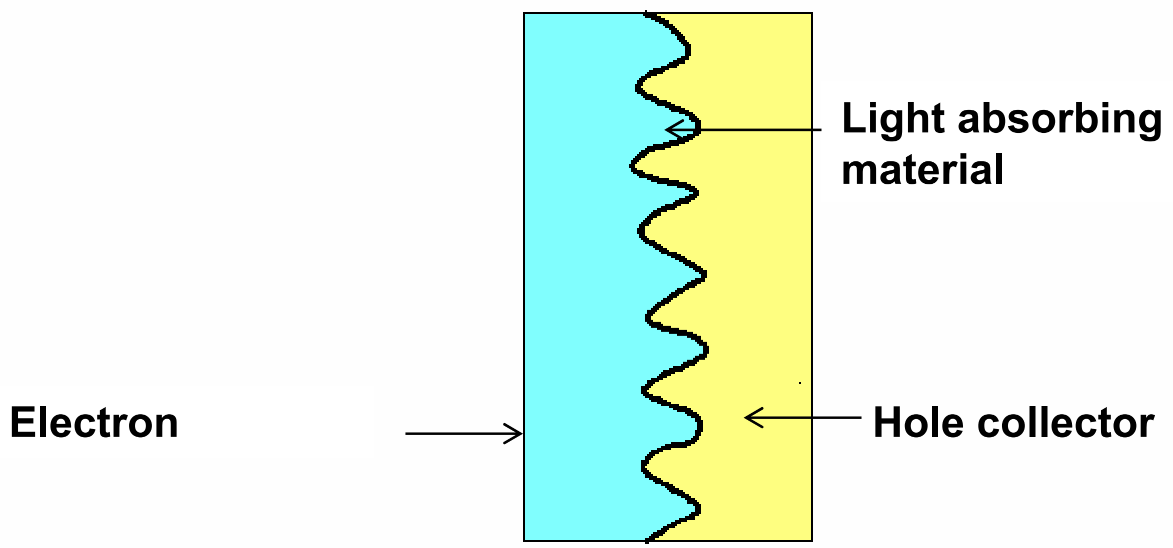
At monolayer coverage quantum and energy conversion efficiencies are very small because of the poor light absorption by the monolayer.

To increase the photon absorption cross-section dye is deposited on the rough electron conducting surface



Dye coverage at monolayer level
Light absorption crosssection increased nearly 1000 fold

Thickness of the light absorbing layer can be made smaller than the exciton or carrier diffusion length $L = (D\tau)^{1/2}$, while maintaining a large optical absorption cross-section



Light absorbing material- dye, semiconductor, Q-dots

Efficiencies (E &Q) of dye-sensitized solar cells

Cells based on electrolytes ~

E~ 10% , Q ~ 85%

Fully solid state cells (solid hole collector) ~
E ~ 4%, Q ~ 60%

Recombination Modes: Dye Sensitized Solar Cells/Photon Detectors

1. Geminate recombination

   $h\nu + D \rightarrow D^* \rightarrow D^+ + e^-$

   $D^+ + e^- \rightarrow D$

2. Recombination of the injected electron with an acceptor at dyed oxide surface

3. Recombination of the injected electron with an acceptor at the exposed conducting glass surface.

Injection and Geminate Recombination Rates

Injection time

$D^* \rightarrow D^+ + e^-$, 10^{-14}- 10^{-15}s

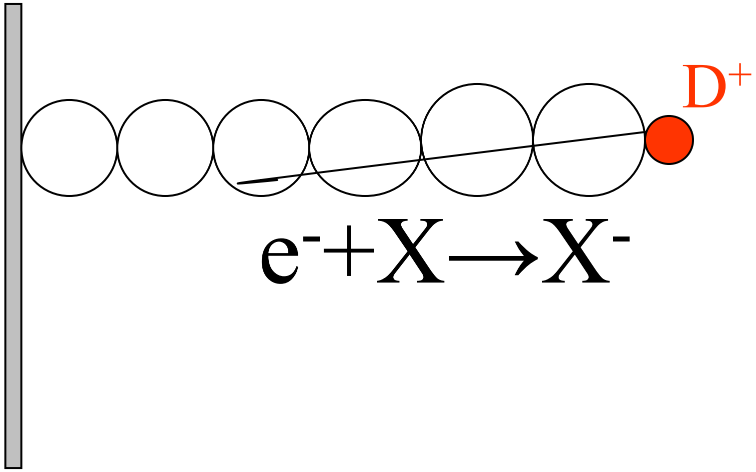
$k = 4\pi^2/h\ [\langle i|H|j\rangle]^2 \rho(E)$?

H = **Semicoductor-Dye Electronic Coupling**

ρ(E) = **Density of States in the CB**

Recombination time **$D^+ + e^- \rightarrow D$, 10^{-5} -10^{-7}s**

Recombination of Electrons with Acceptors During Transit

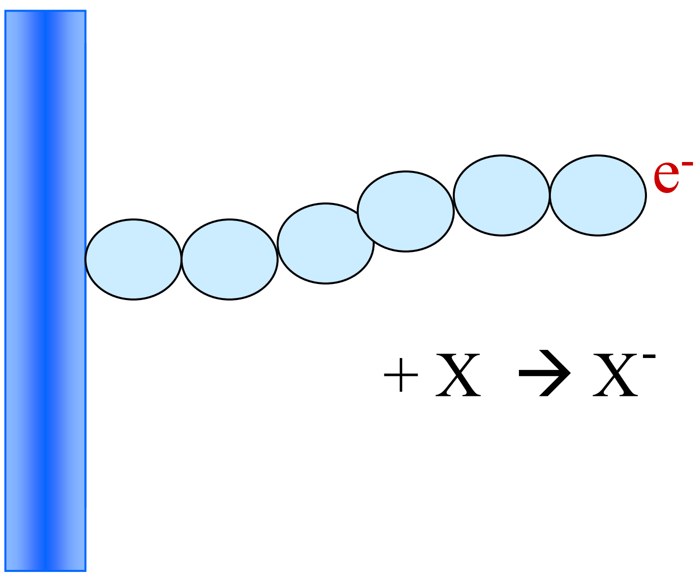


$e^- + X \rightarrow X^-$

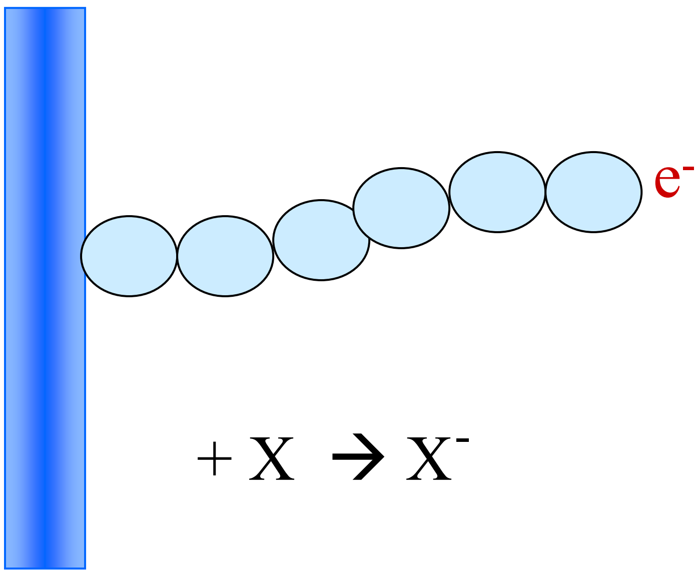
Recombination rate =κ

Recombination Time =$\kappa^{-1} = \tau$

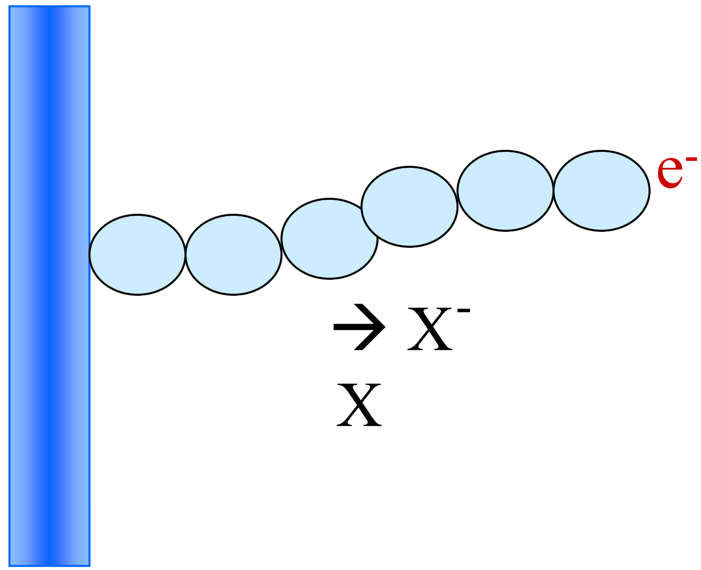
Mean free path = $(D\tau)^{1/2}$



Recombination after leakage from the nano-particle surface



Recombination at the back contact

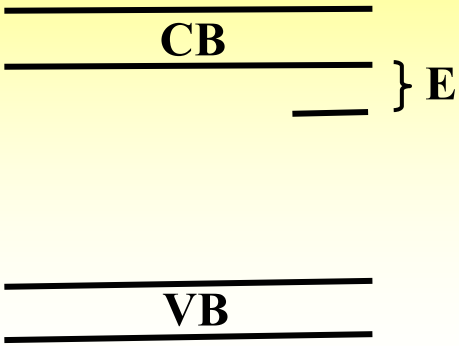


Surface trap mediated recombination

Problem of Surface Traps

1. Surface trap mediated recombination is very severe
2. Trapping and detrapping slows down transport (reduces diffusion coefficient)
3. Trapping/Detrapping generate noise

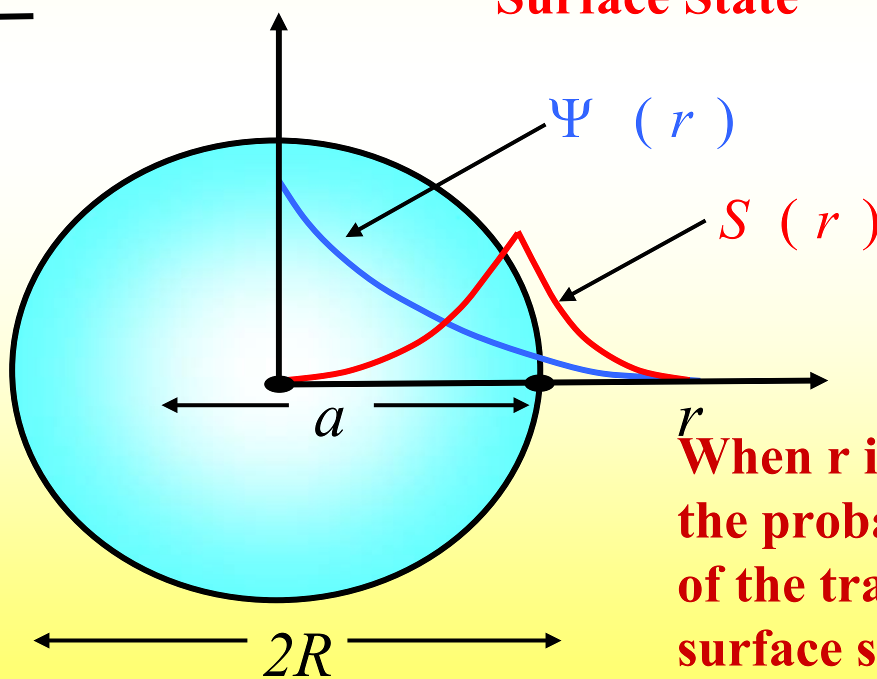
Transition of a trapped electron to a surface state



Trapped Electron $\Psi(r) \sim e^{-r/a}$

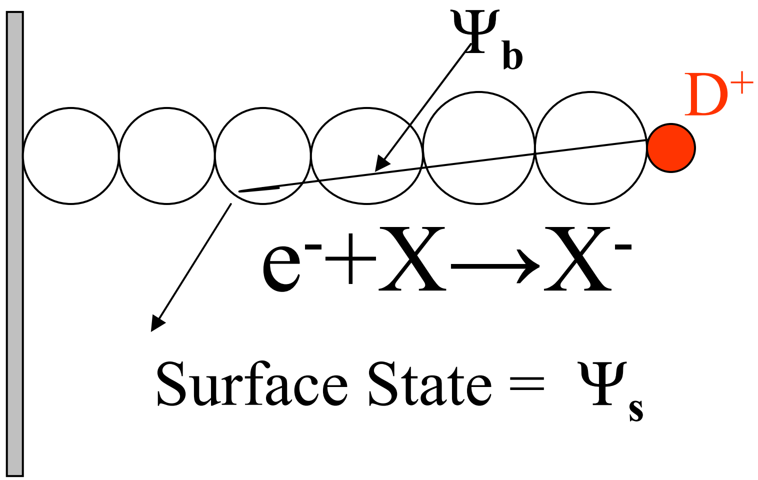
$$a = h\,(2\,m^*\,E)^{-1/2}$$

Surface State $\sim S(r)$



When r is comparable to *a* the probability of transition of the trapped electron to a surface state is high

Recombination of Electrons with Acceptors During Transit



Recombinations are generally mediated by surface states

Recombination Rate ~ (Ψ_s, Ψ_b)

We are not certain whether Ψ_b the wave function of electron in the bulk of the semiconductor is conduction band state or a trapped state

1/f Noise in Mesoscopic Semiconductor films

At constant voltage ,current exhibits 1/f (f=frequency)noise

This noise is quite sensitive to trapping-detrapping of carriers

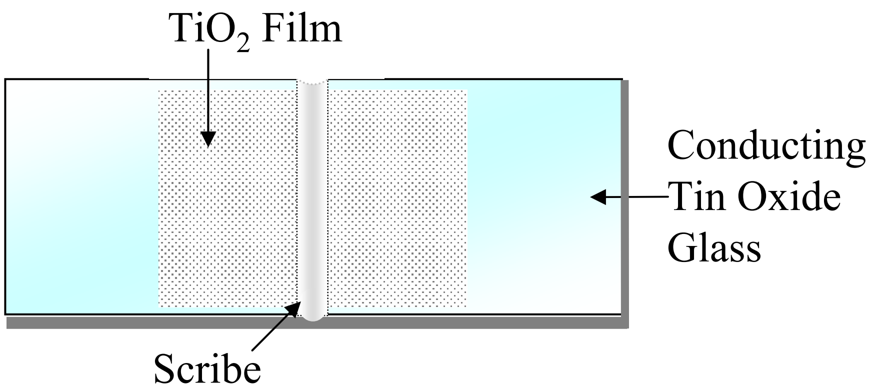
The fluctuating current is of the form

$I(t) = I_0 + X(t)$ where I_0 is the mean and we define $S(f)$ as

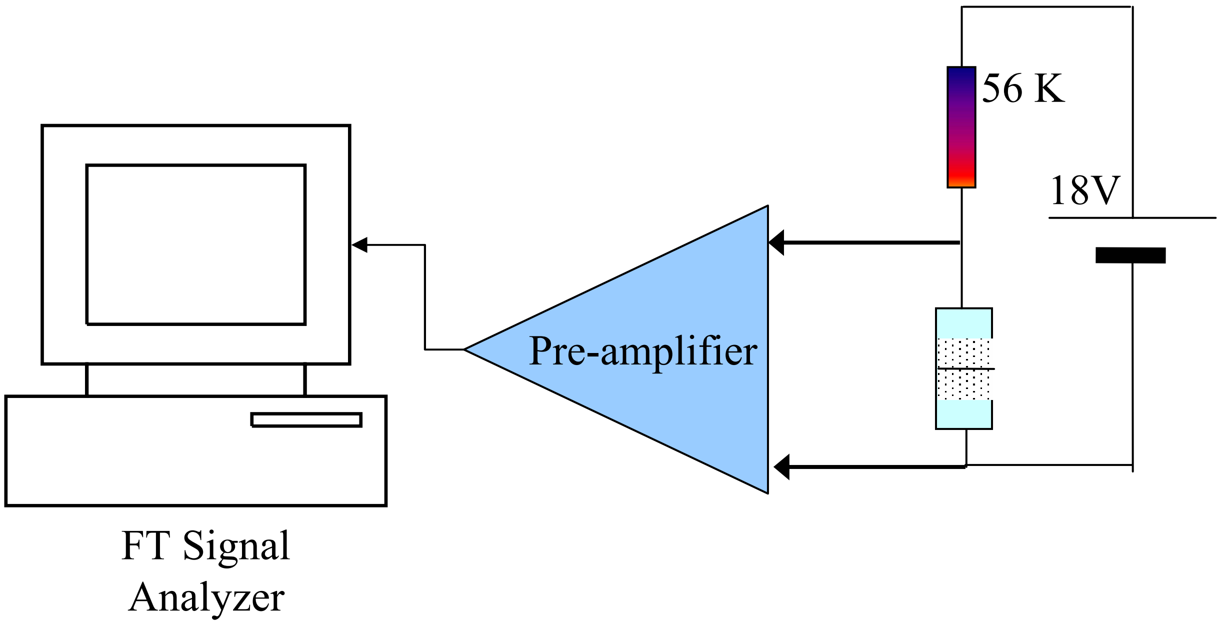
$$S(f) = Lim_{T \to \infty} \left(\frac{1}{2T} \left| \int_{-T}^{T} X(t) e^{-2\pi i f t} dt \right|^2 \right)$$

S(f) gives the noise power spectrum as a function of f

A schematic diagram illustrating (a) sample geometry used for the noise measurement. (b) The circuit used for the noise measurement.



(a)



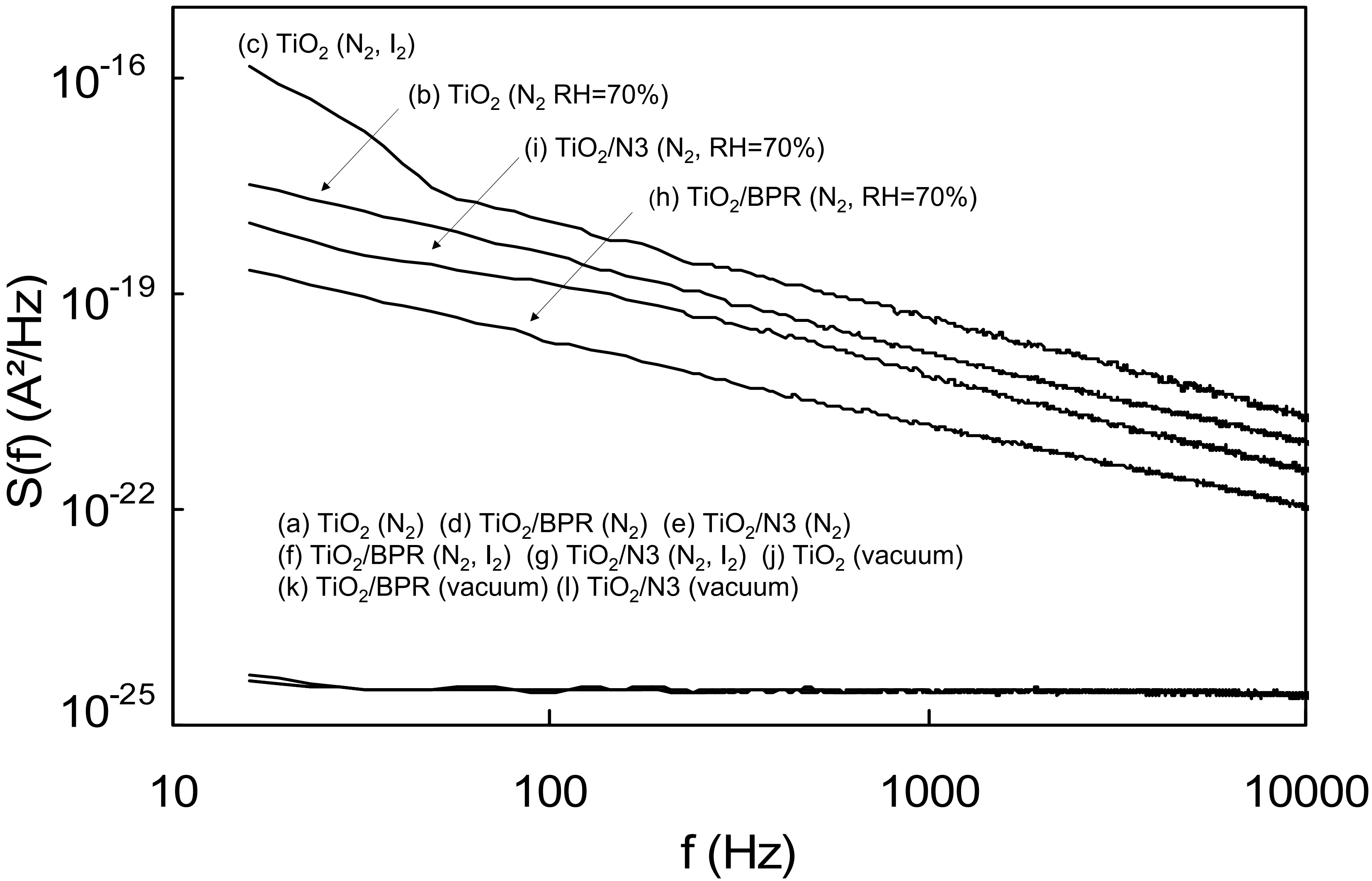
(b)

S(f) generally satisfy Hoog's Formula

$$S(f) = \frac{A I_0^2}{f^{\delta}}$$

The constant A measures the level of noise and δ is an exponent close to unity.

Noise spectra at 23°C of, **(a)** bare TiO2 film in N2. **(b)** bare TiO2 film in N2 at RH ~70 %. **(c)** bare TiO2 in a N2 saturated with I2 vapor. **(d)** TiO2/BPR in N2. **(e)** TiO2/N3 in N2. **(f)** TiO2/BPR in N2 saturated with I2. **(g)** TiO2/N3 in N2 saturated with I2. **(h)** TiO2/BPR in N2 at RH ~70 %. **(i)** TiO2/N3 in N2 at RH ~70%.



The values of parameters A and δ for different systems obtained by fitting noise data to the formulae (1),

biasing voltage = 18 V : $I_o = 3.2\times10^{-4}$ A.

sample	δ	A
TiO_2 (vacuum)	0	4.4×10^{-18}
TiO_2 (N_2)	0	4.4×10^{-18}
TiO_2/BPR (vacuum)	0	4.4×10^{-18}
TiO_2/N3 (vacuum)	0.	4.4×10^{-18}
TiO_2/BPR (N_2)	0	4.4×10^{-18}
TiO_2/N3 (N_2)	0	4.4×10^{-18}
TiO_2(N_2 ,RH = 70%)	1.25	8.8×10^{-10}
TiO_2/BPR (N_2, RH= 70%)	1.15	4.4×10^{-11}
TiO_2/N3 (N_2 , RH = 70%)	1.30	5.7×10^{-10}
TiO_2 (N_2 , saturated I_2 vapor)	1.37	5.8×10^{-9}
TiO_2/BPR (N_2 , saturated I_2 vapor)	0	4.3×10^{-18}
TiO_2/N3 (N_2 , saturated I_2 vapor)	0	4.4×10^{-18}

Results of the Noise Measurement

1. TiO_2 film in vacuum or N_2 no 1/f noise
2. TiO_2 film in N_2 with traces of I_2 intense 1/f noise
3. Dyed TiO_2 film in N_2 with iodine no 1/f noise

Electron acceptor states created by adsorbed iodine creates 1/f noise. The dye passivates acceptor states.

When the nanocrystalline surface is bonded with a suitable dye , the trapping sites are passivated.

1/f noise suppressed

Recombination suppressed

Electron transport facilitated ($D_{dye} >> D_{bare}$)

Recombination in Dye-sensitized Devices

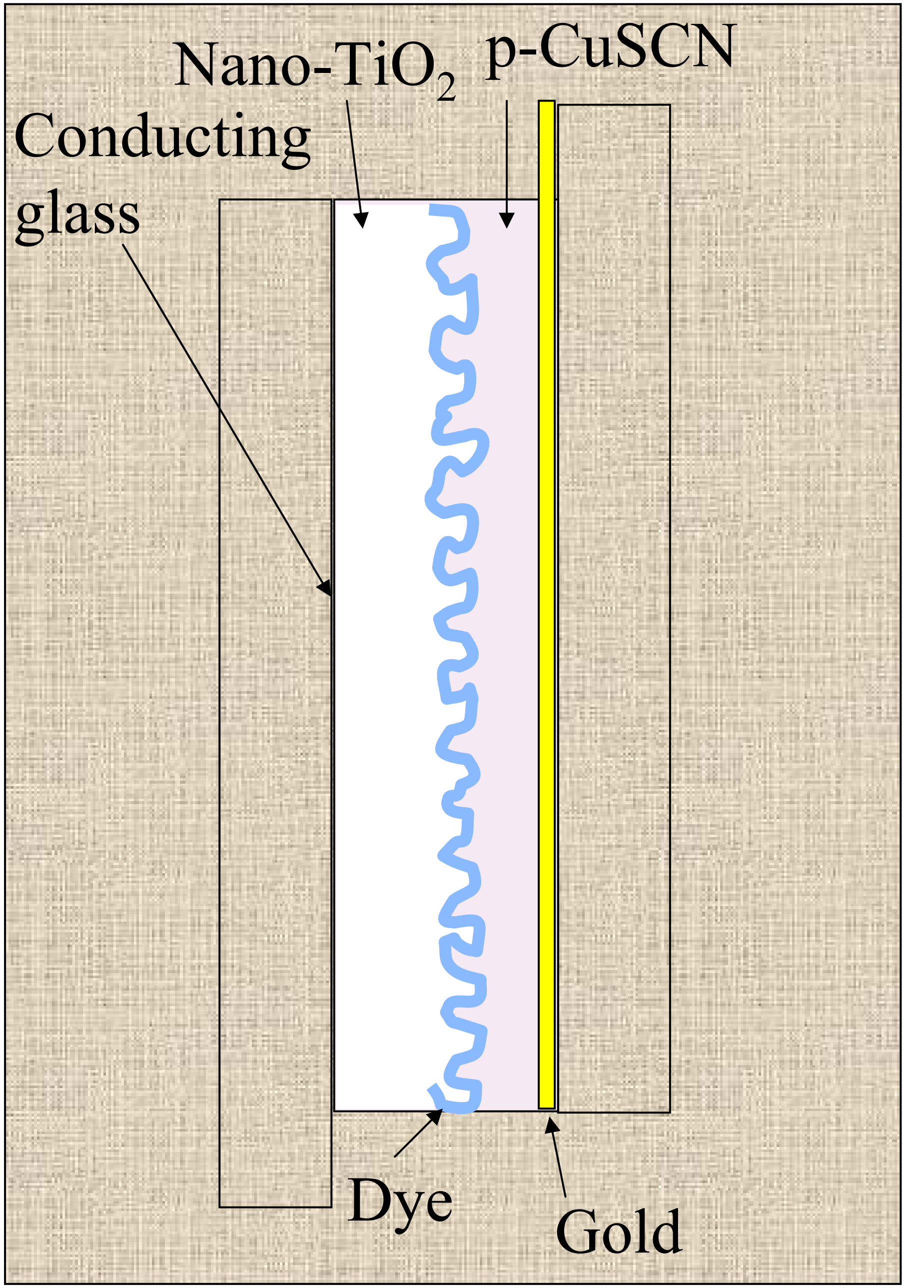
Surface traps that generate 1/f noise are also the recombination sites.

Conclusion from Noise Experiments

Nanocrystalline oxide films are heavily populated with defects, surface states ,adsorbed species etc, that act as trapping (recombination) sites. Passivation by dye adsorption clears most of these traps.

Possible applications – Solar Cells, Photon Detectors.

Dye-sensitized NIR detector



Response time $\tau \sim L^2/D$

L= Film thickness, D = Diffusion coefficient

Detectivity ~ 10^{11} cm $Hz^{-1/2}W^{-1}$ (812 nm)

Detectivities of the same order for some dyes absorbing in the region 1000 nm

Responsitivities are rather low ~ 10^{-3} A/W

Strategies for improvement

Design dyes to achieve the following

1. Peak absorption
2. Fast injection slow geminate recombination
3. Attach ligands to passivate trapping sites

Conclusion

High band-gap mesoscopic semiconductors

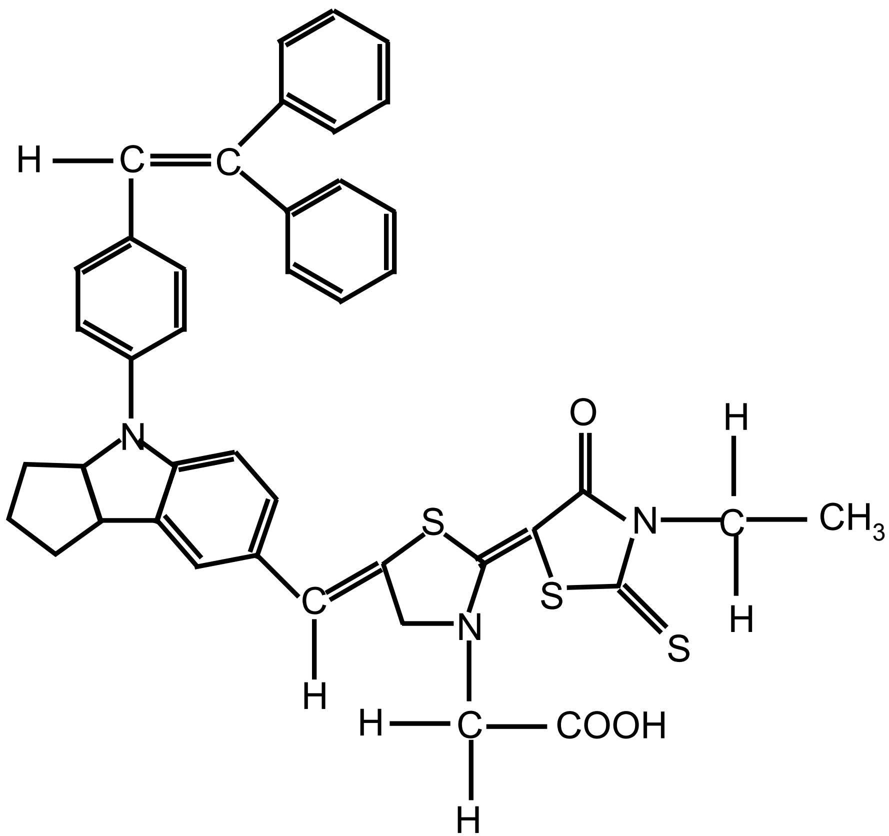
1. **Insensitive to visible/IR**
2. **Slow carrier transport**
3. **Noise**
4. **Recombination of photogenerated carriers**

All the above ills can be cured in one stroke by bonding the surface with a suitably designed dye

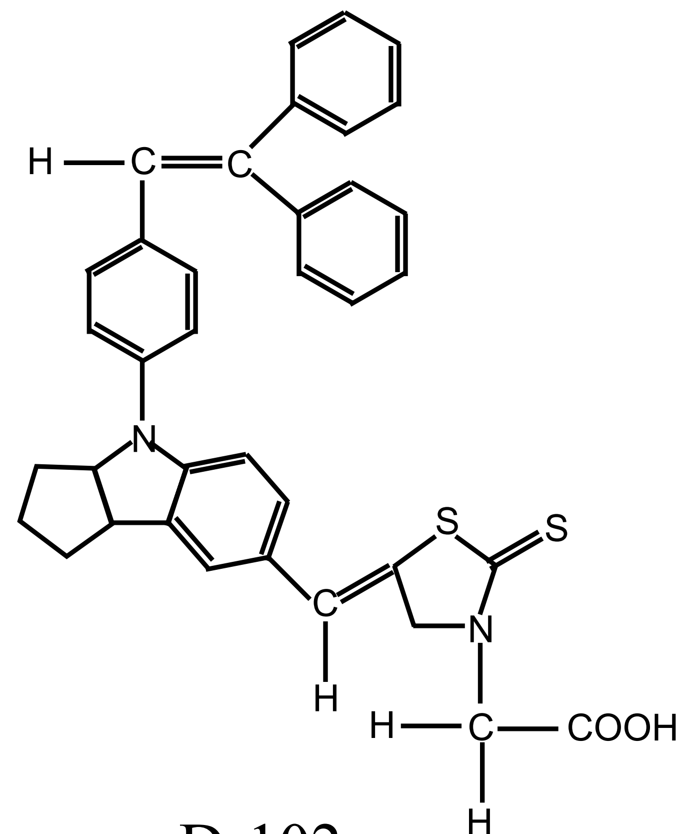
Cells based on Indoline Dyes

- **Indoline organic dyes give high conversion efficiencies ?**
- **Understanding of their properties and mode of interaction with TiO_2 likely to give very important clues**

Structural Formula of the Indoline dyes D-149 and D-102



D-149



D-102

The Secret of Indolines?

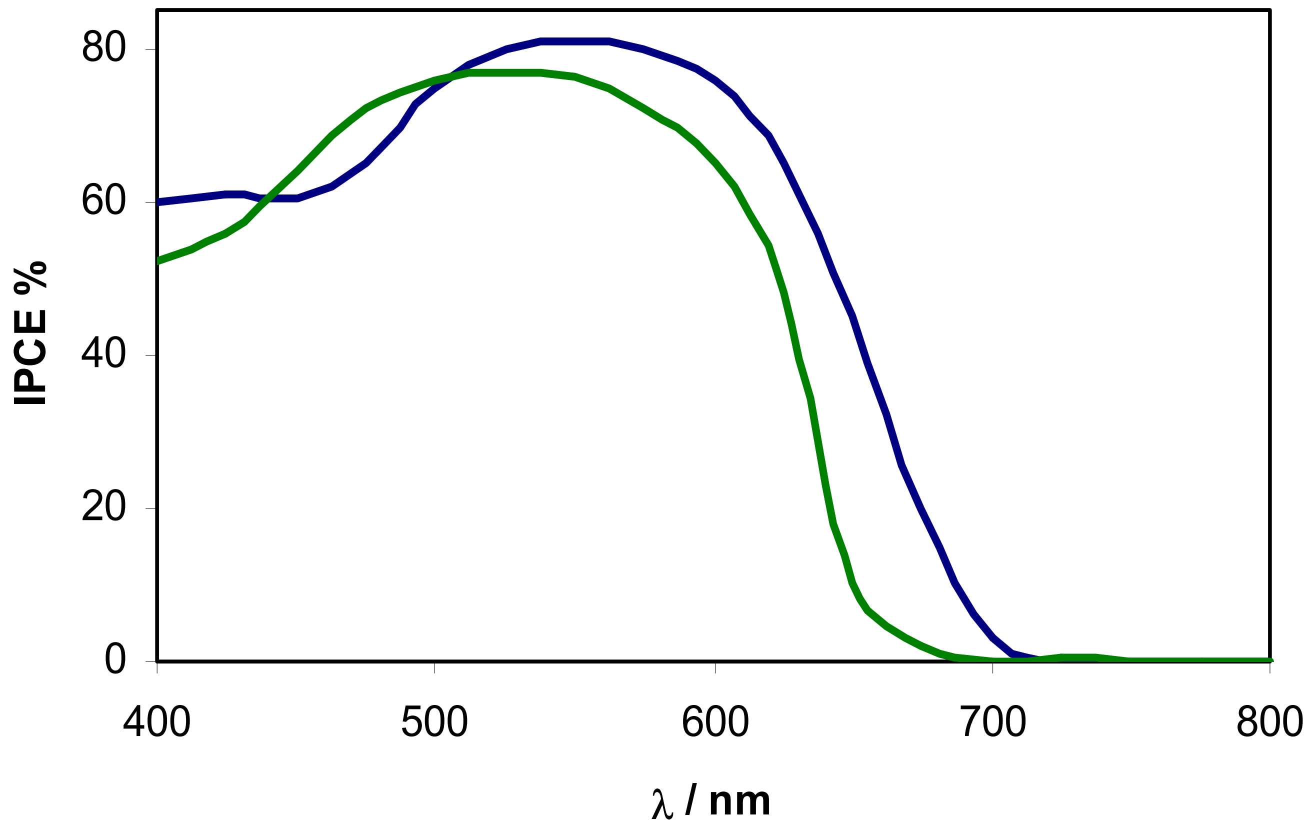
Anchorage via carboxylate ligand facilitate electron injection.

It seems that basic nitrogen sites in indoline passivates electron accepting acidic sites on TiO_2 . Thus recombination and noise suppressed.

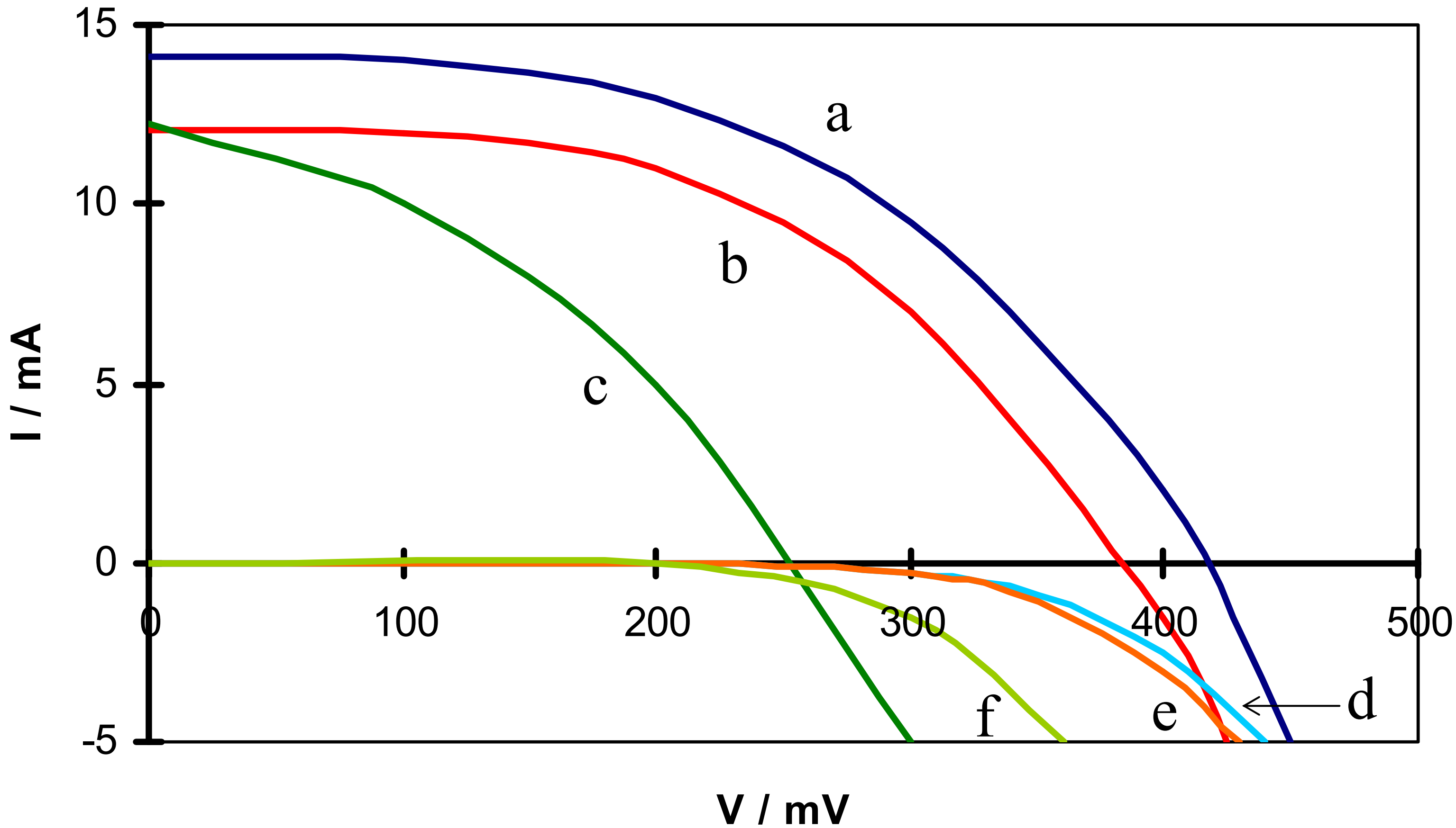
Indoline like structures can be made to absorb in the NIR region

Photocurrent Action spectra of SnO_2 cells sensitized with

(a) D-149 and (b) D-102



I-V Characteristics of SnO_2 cells sensitized with (a) D-149 (b) D-102 and (c) N719 and Dark I-V Characteristics of SnO2 cells sensitized with (d) D-149 (e) D-102 and (f) N719



I-V Parameters of SnO_2 cells sensitized with indoline and Ru-bipyridyl dyes

Dye	**J_{sc}** ***mAcm^{-2}***	**V_{oc}** ***mV***	**η** **%**	**FF**
D-149	*14.1*	*409*	*2.8*	*0.49*
D-102	*11.9*	*380*	*2.2*	*0.50*
N-719	*12.1*	*262*	*1.2*	*0.37*

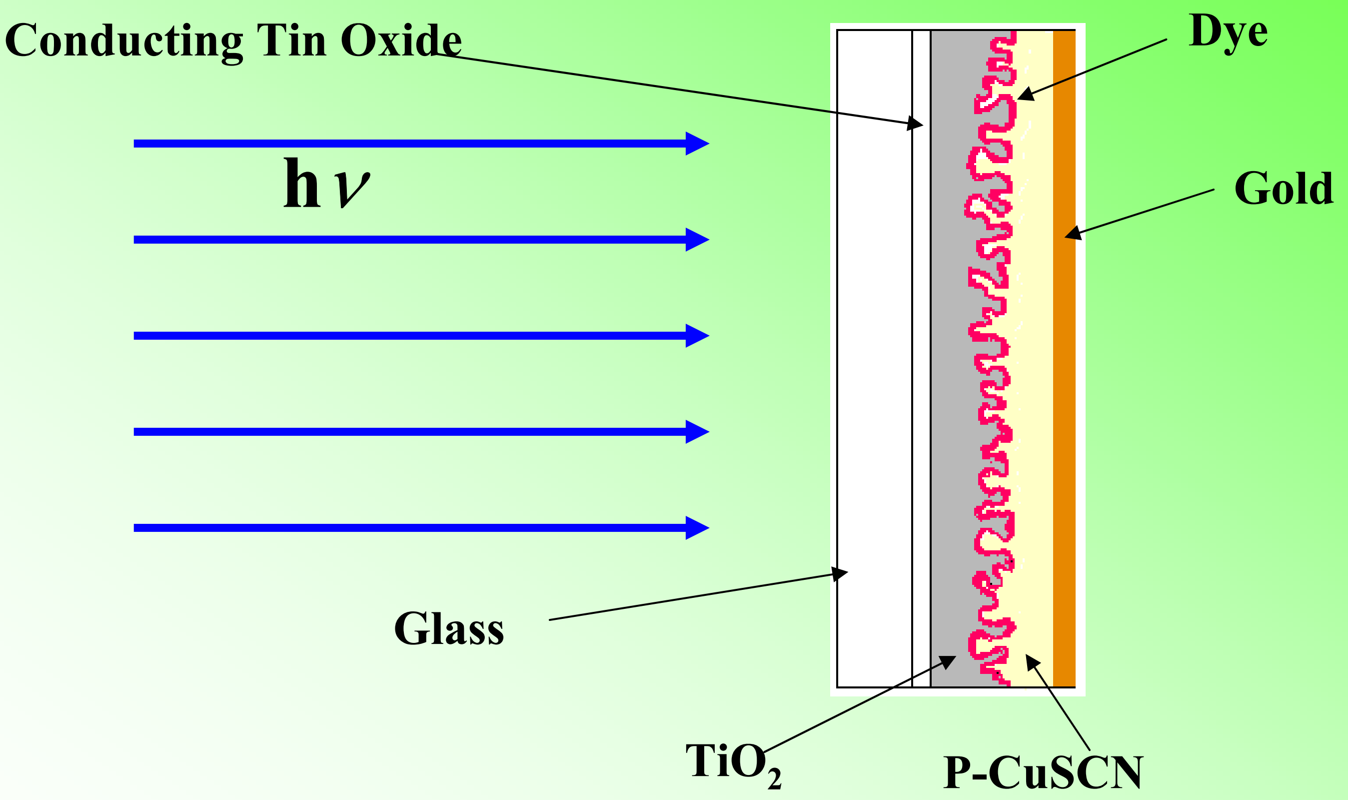
Indoline vs Ru dyes on SnO_2

SnO_2 based dye-sensitized cells are more susceptible to recombination than TiO_2 cells.

With SnO_2 indolines give efficiencies higher than that Ru bipyridyl dyes

It seems that indoline dyes passivates SnO_2 surface more effectively closing the recombination sites

Dye-sensitized NIR Detector



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