Simple techniques to enhance semiconductor characteristics in solar energy conversion processes

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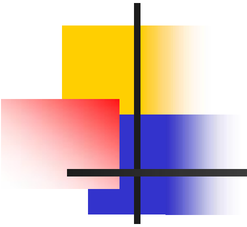
Welcome and thanks

- Welcome to all audience
- Welcome to all participants
- Thanks to organizing committee



This work has been conducted in collaboration with many colleagues and students including:

*Najah N. University: Subhi Salih, Iyad Sadeddin, Samar Shakhshir, Wajdi Attereh, Moayyad Masoud, Nidal Zaatar, Amer Hamouz,

- Birzeit: Najeh Jisrawi
- France: Guy Campet
- USA: John Turner

Results of this work have been published in the following:

- H. S. Hilal* and J. A. Turner, “CONTROLLING CHARGE-TRANSFER PROCESSES AT SEMICONDUCTOR/LIQUID JUNCTIONS”. J. Electrochim. Acta, 51 (2006) 6487–6497.
- H. S. Hilal*, M. Masoud, S. Shakhshir, N. Jisrawi, “n-GaAs Band-edge repositioning by modification with metalloporphyrin/polysiloxane matrices” Active and Passive Electronic Components, 26(2003), 1. [UK, English].
- H. S. Hilal*, M. Masoud, S. Shakhshir and N. Jisrawi, “Metalloporphyrin/polysiloxane modified n-GaAs surfaces: Effect on PEC efficiency and surface stability”, J. Electroanal. Chem., 527, (2002) 47-55.
- H. S. Hilal*, I. Sadeddin, S. Saleh, Elisabeth Sellier and G. Campet, Modification of n-Si characteristics by annealing and cooling at different rates, Active and Passive Electronic Components, 26(2003)213.
- H. S. Hilal*, S. Saleh, I. Sadeddin and G. Campet, "Effect of Annealing and Cooling Rates on n-GaAS Electrode Photoelectrochemical Characteristics", Active and Passive Electronic Components, 27(2), (2004) 69-80.
- H. S. Hilal*, W. Ateereh, T. Al-Tel, R. Shubaitah, I. Sadeddin and G. Campet, Enhancement of n-GaAs characteristics by combined heating, cooling rate and metalloporphyrin modification techniques, Solid State Sciences, 6, (2004)139-146. J. PORTIER, H. S. HILAL*, I. SAADEDDIN, S.J. HWANG and G. CAMPET , “THERMODYNAMIC CORRELATIONS AND BAND GAP CALCULATIONS IN METAL OXIDES”, Progress in Solid State Chemistry, 32 (2004/5), 207.
- H. S. Hilal*, L. Z. Majjad, N. Zaatar and A. El-Hamouz, DYE-EFFECT IN TiO2 CATALYZED CONTAMINANT PHOTODEGRADATION: SENSITIZATION VS. CHARGE-TRANSFER FORMALISM, Solid State Sciences, 9(20078)9-15.
- H. S. Hilal, J. A. Turner, and A. J. Frank, " Surface-modified n-GaAs with tetra(-4-pyridyl)porphirinatomanganese(III)", 185th Meeting of the Electrochemical Soc., San Francisco, Ca., May 22-27, (1994).
- H. S. Hilal, J. A. Turner, and A. J. Frank, " Surface-modified n-GaAs with tetra(-4-pyridyl)porphirinatomanganese(III)", 185th Meeting of the Electrochemical Soc., San Francisco, Ca., May 22-27, (1994).
- H.S.Hilal and J.Turner, Electrochimica Acta xxx (2006)

Strategic Objectives

- Utilize solar energy in large scale economic environmentally friendly processes, such as:
- Part (I) Electricity production
- Part (II) Water purification by degrading contaminants

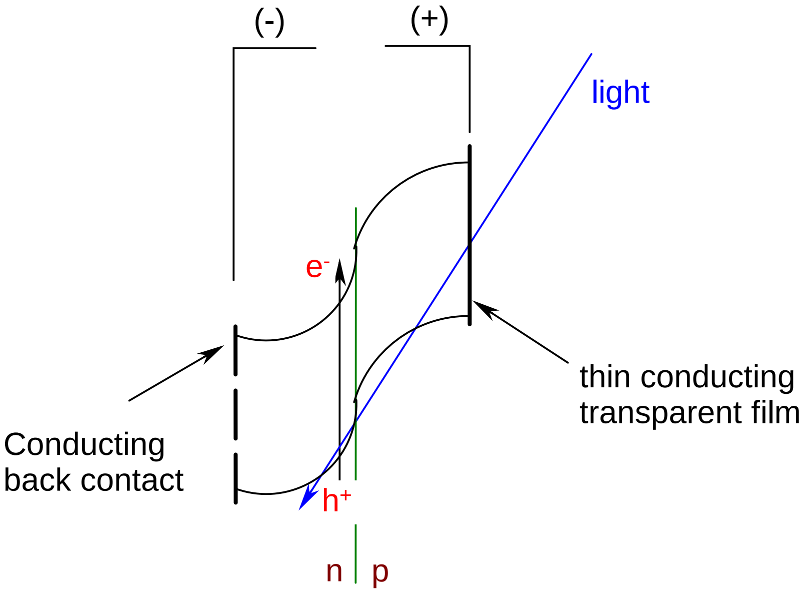
Part I: Light-to-electricity

- LIGHT-to-electricity CONVERSION TECHNIQUES
- p-n junctions
- PEC junctions: Two types

Regenerative

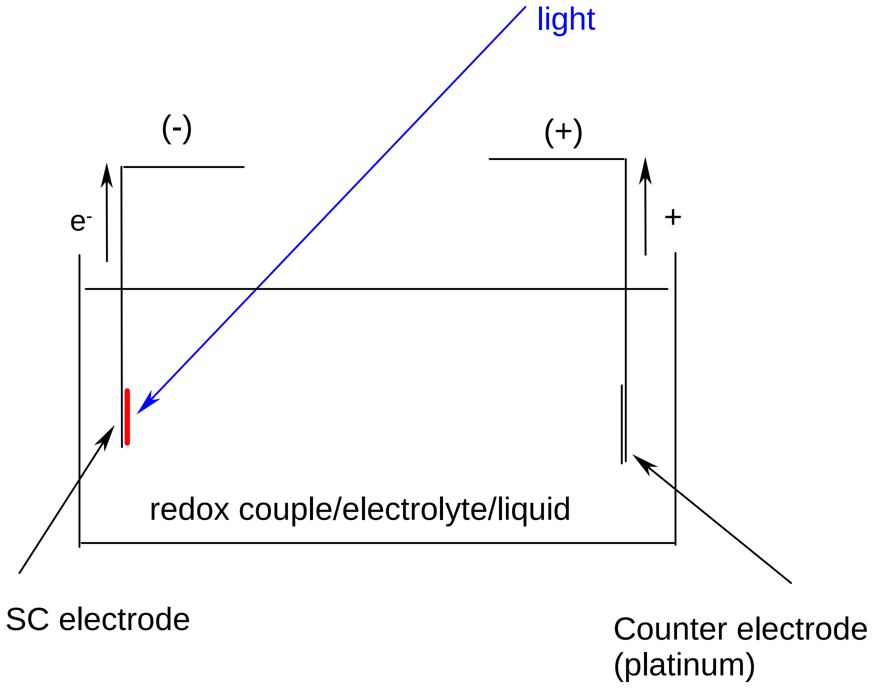
Non-regenerative

p-n junctions PV devices: Priciple, advantages and disadvantages



light to electricity
in p-n junctions

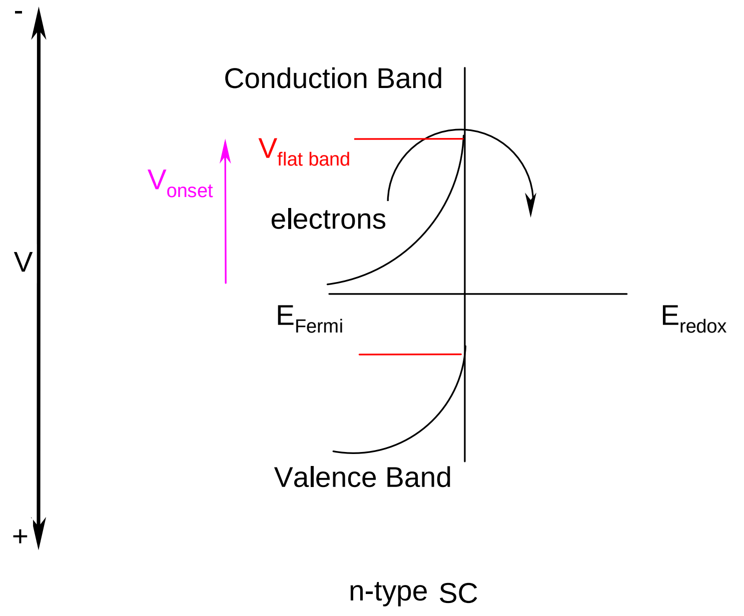
Photoelectrochemical (PEC) Devices: Principles, advantages and disadvantages



Photoelectrochemical cell

Dark-Current Formation

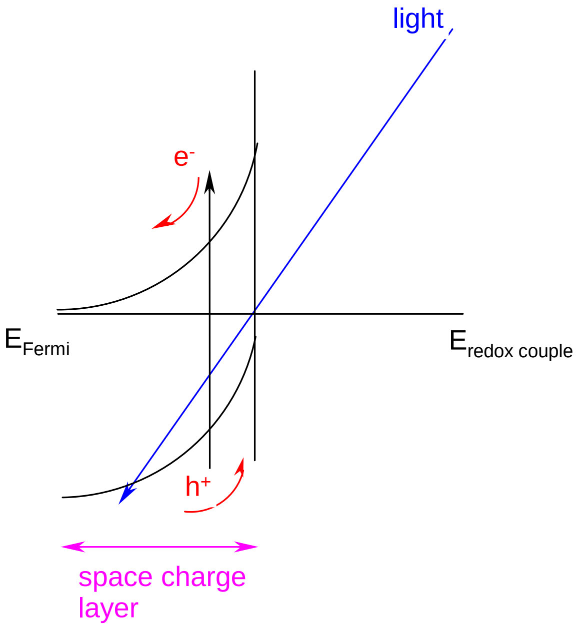
(Band-edge Flattening is needed here)



Dark Current:
Demands negative bias

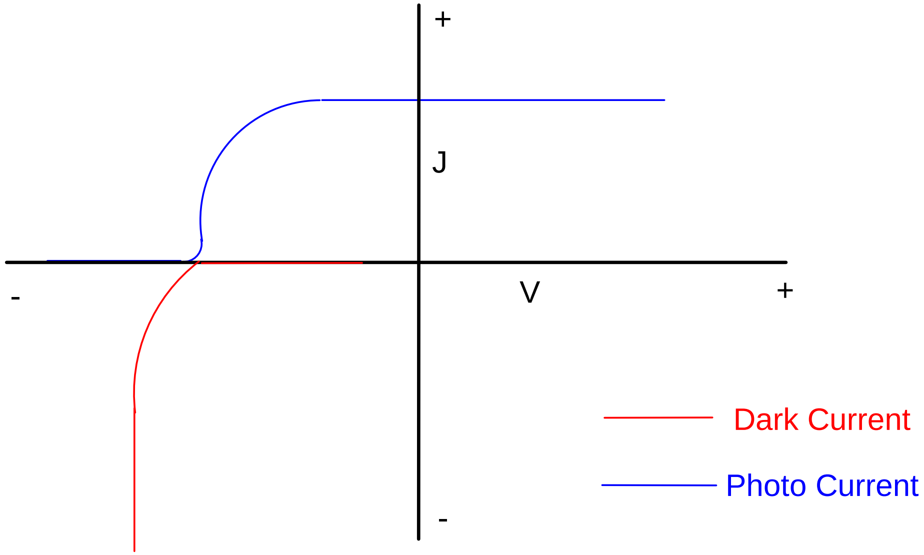
Photocurrent Formation:

(Band-edge bending is needed here)



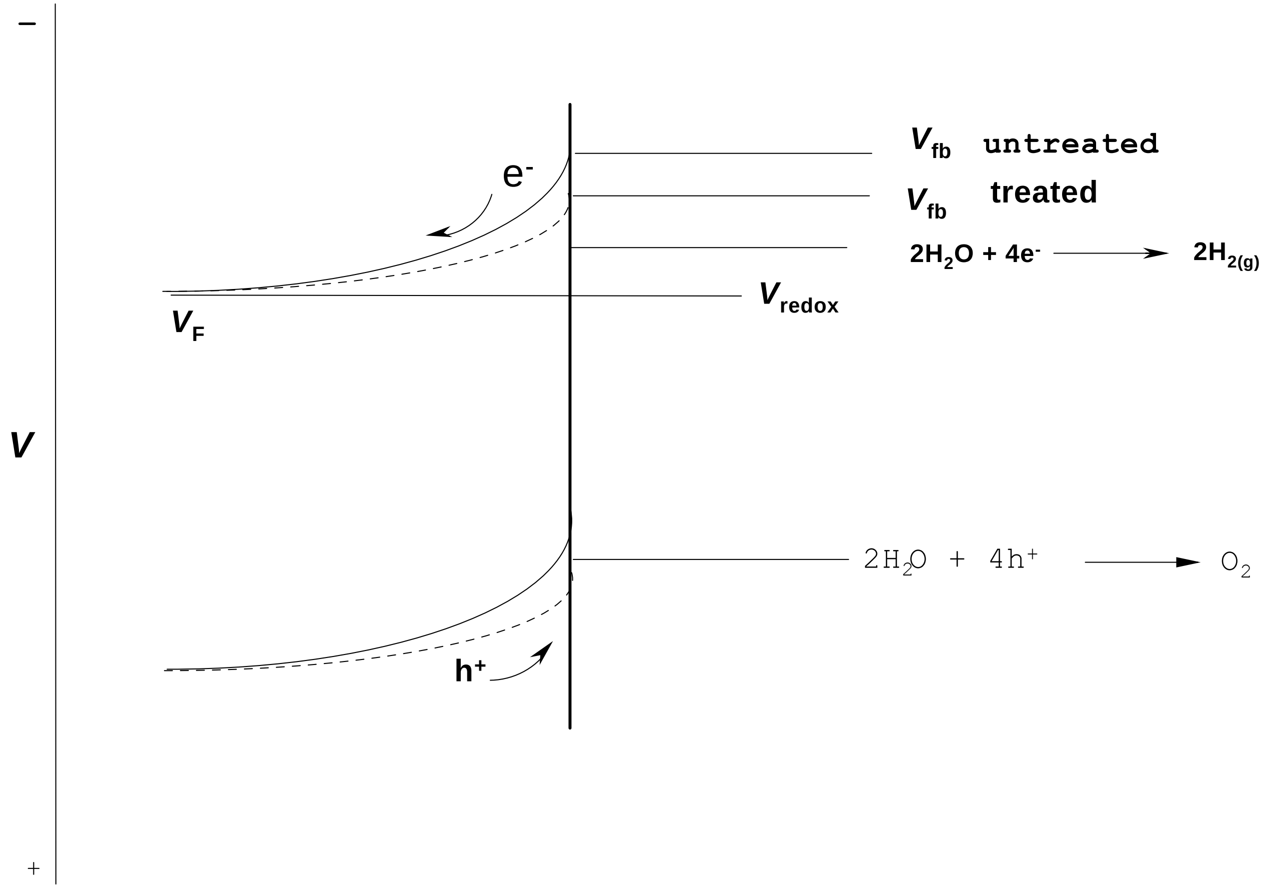
Photoelectrochemical Principles: Photo current resulting from light excitation of electrons)

Total current vs. Potential



Typical plots of current vs. applied potential
in PEC operations

Band-Edge Position Shifting



Scheme I

Earlier Modification Activities

- Literature: Attachment of conjugated polymers, such as polythiophenes

  -stability became higher

  -current became smaller, and efficiency became lower

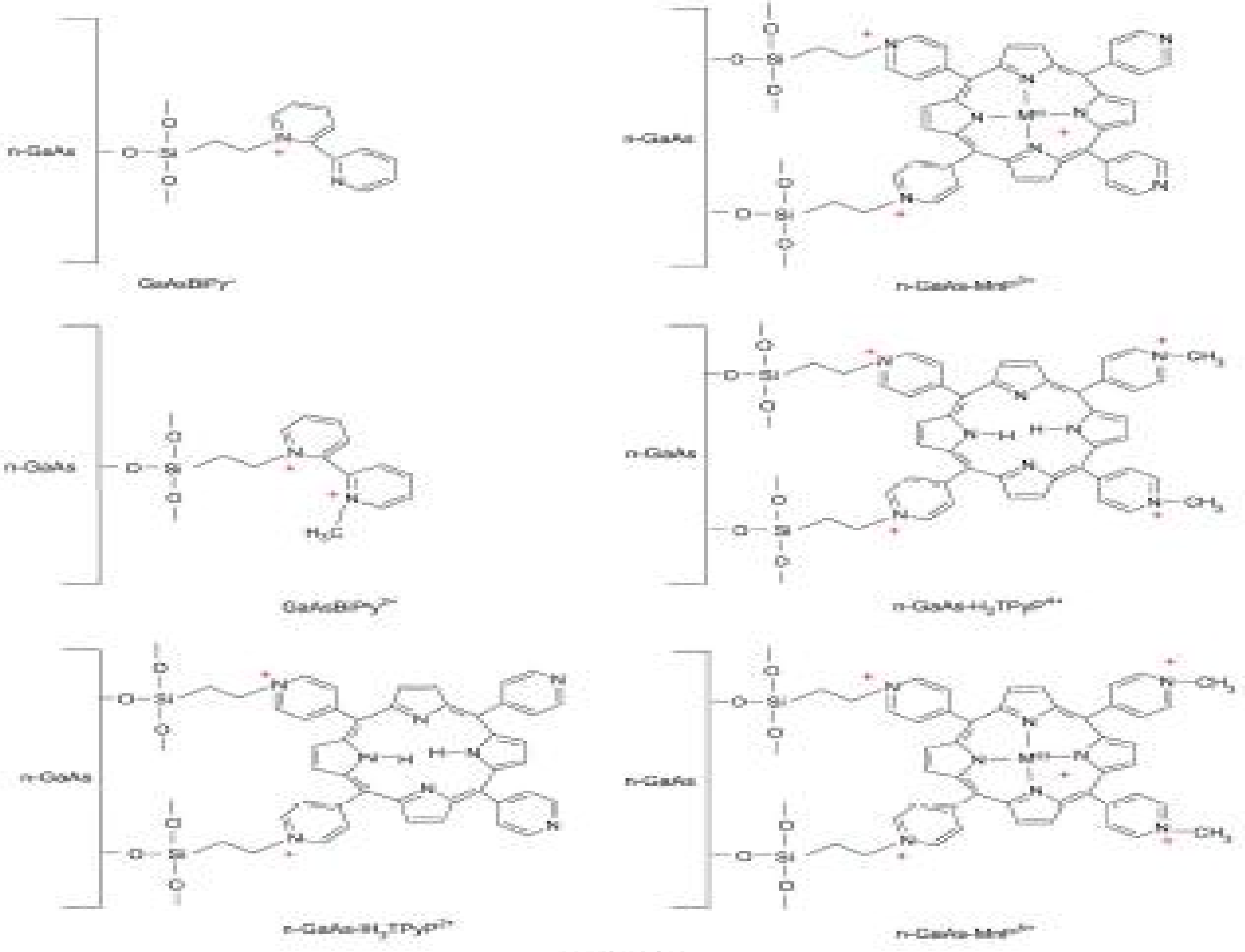
  -polymer peeling out difficulties

- Our earlier Technique: Attachment of positive charges

Earlier modifications: Metalloporphyrine treatment of semiconductor surface (submonolayer coverage) using chemical bonding

(H.S.Hilal, J.A.Turner, and A.J.Frank, 185th Meeting of the Electrochemical Soc., San Francisco, Ca., May 22-27, (1994); S.Kocha, M.Peterson, H.S.Hilal, D.Arent and J.Turner, Proceedings of the (1994) USA Department of Energy/NREL Hydrogen Program Review, April 18-21)

. Electrochim. Acta 2006.



Scheme 3.

Photoluminescence enhancement

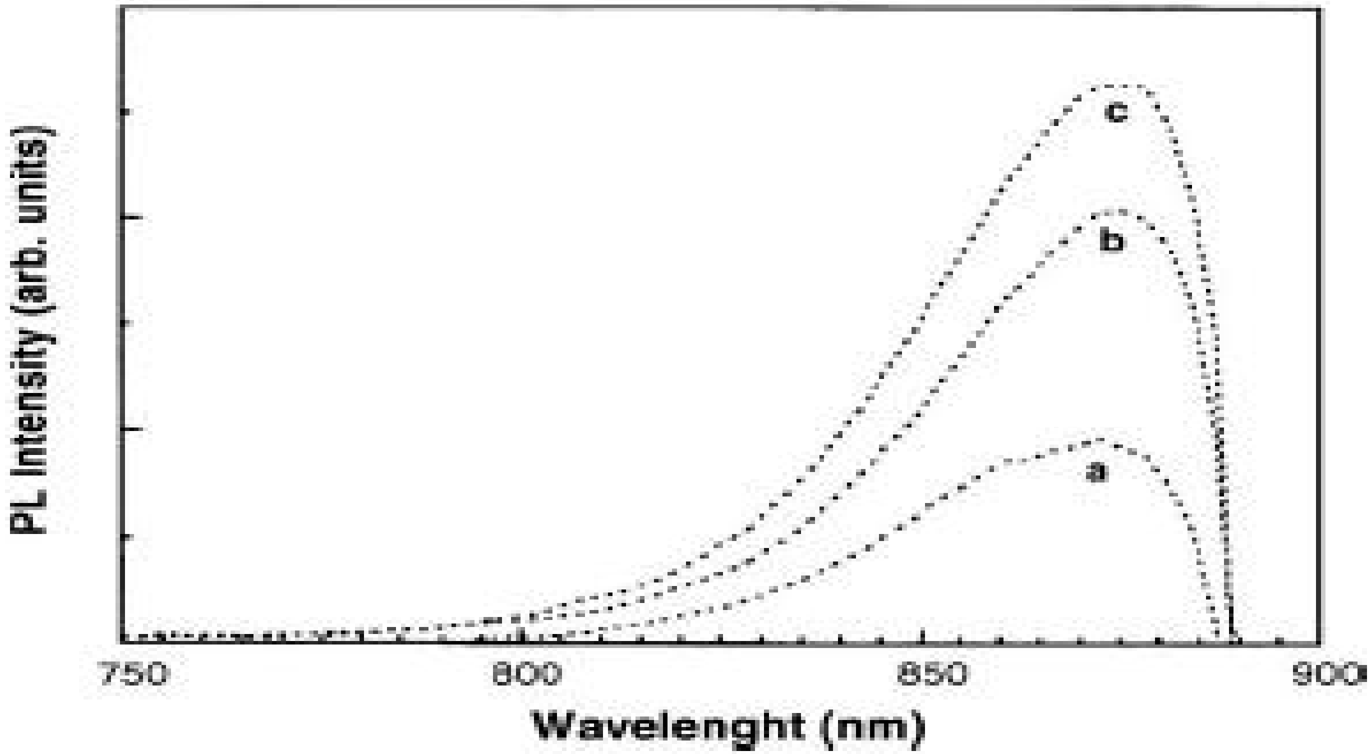


Fig. 2. PL intensity enhancement of n-GaAs by surface modification. (a) Unmodified surface; (b) GaAs-Silyl(Cl); (c) GaAs-MnP^{3+}. Excitation wavelength was 500 nm.

Mott-Schottky Plots after modification

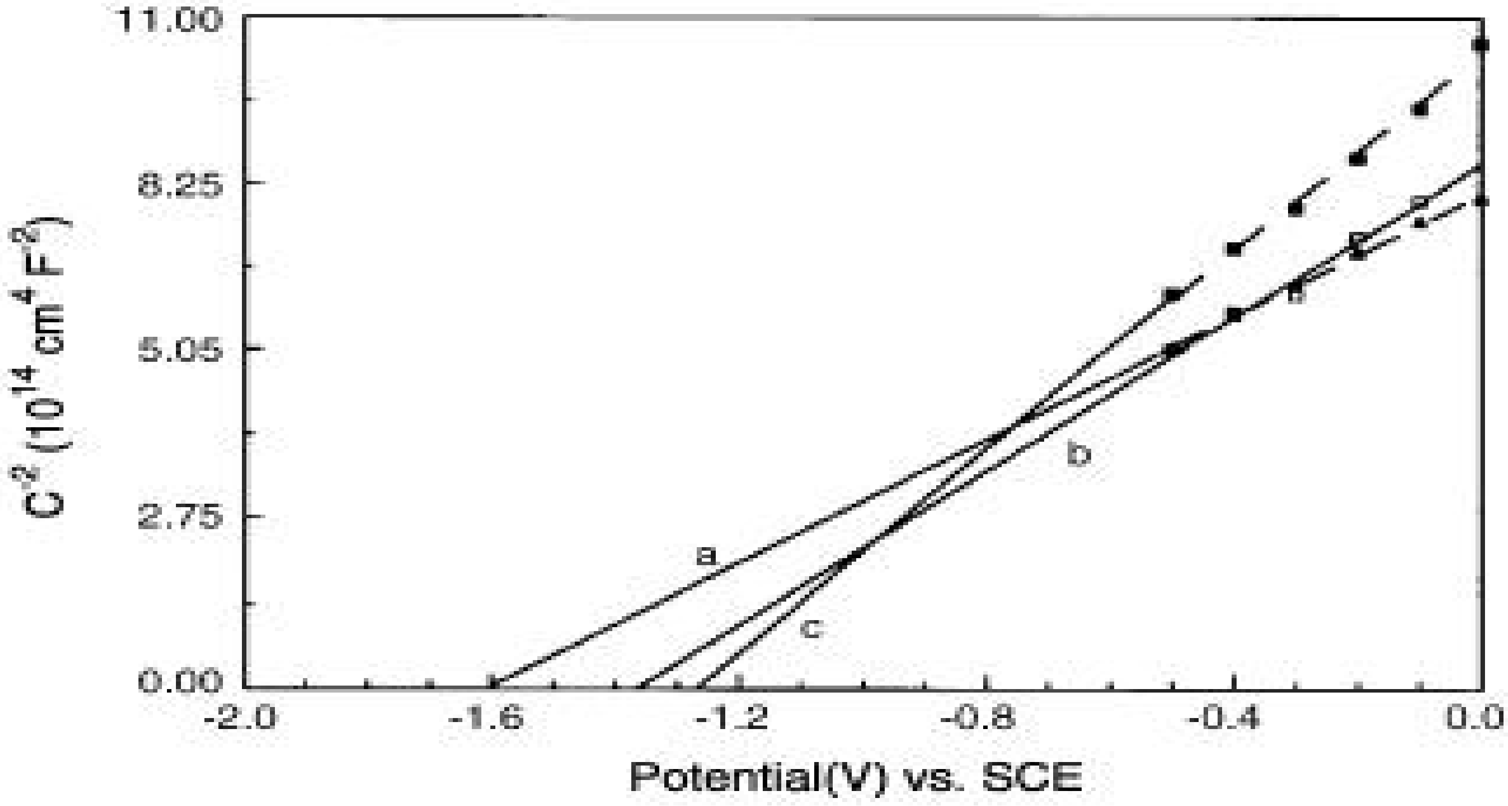


Fig. 3. n-GaAs flat-band potential shifting by surface modification. *C*–*V* (dark) plots measured for n-GaAs: (a) unmodified surface (b) GaAs-Silyl(Cl); (c) GaAs-MnP^{3+}. Measurements conducted using LiClO$_{4(aq)}$ (0.1 M), no added redox couples, pH 6.22 vs. SCE reference.

Fig. 4. n-GaAs flat-band potential shifting by surface modification; in the dark (A), and under illumination (B). Measurements conducted using $LiCO_{4(aq)}$ (0.1 M), no added redox couples. (a) Unmodified n-GaAs and (b) GaAs-MnP^{3+}.

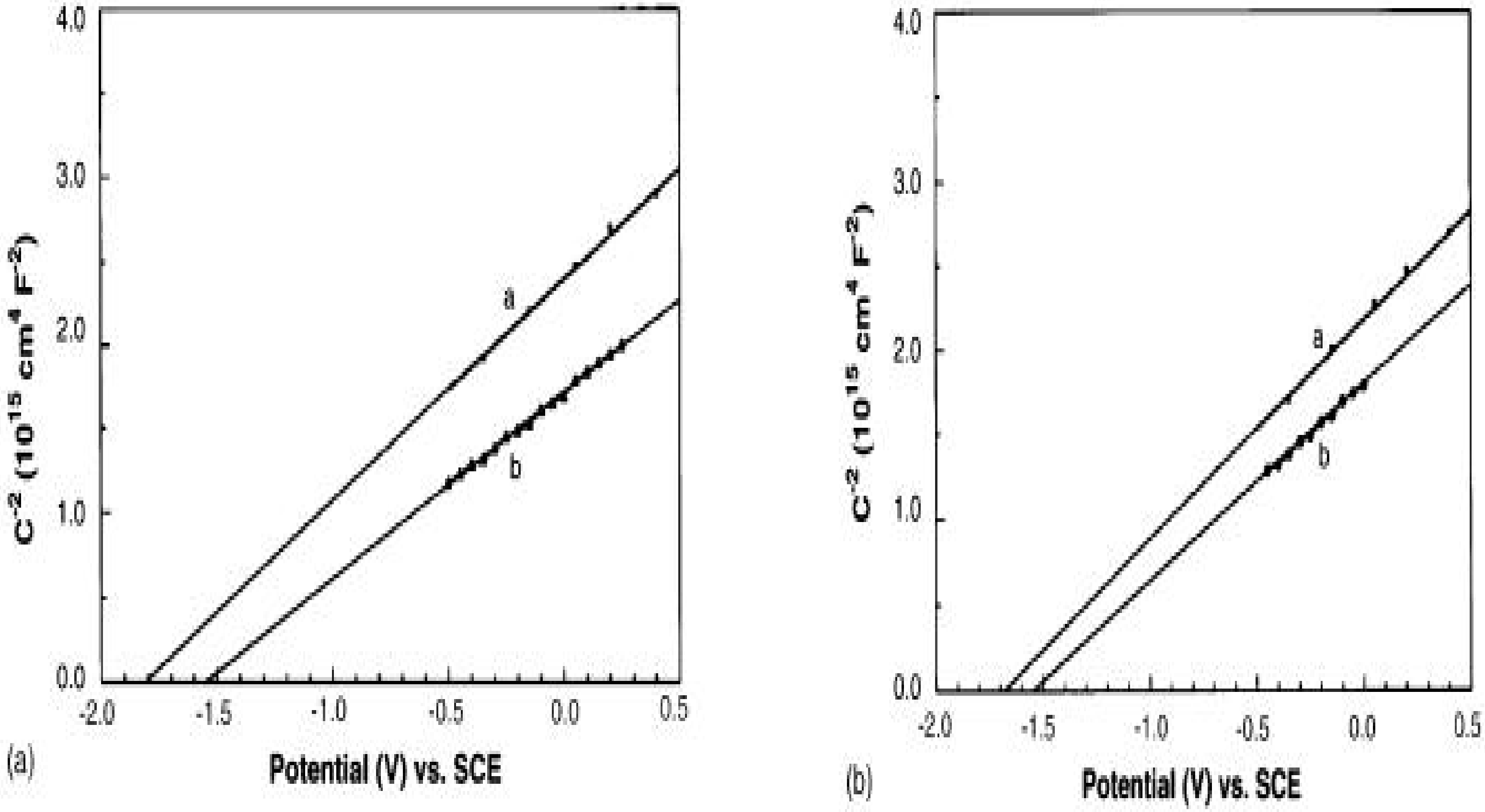
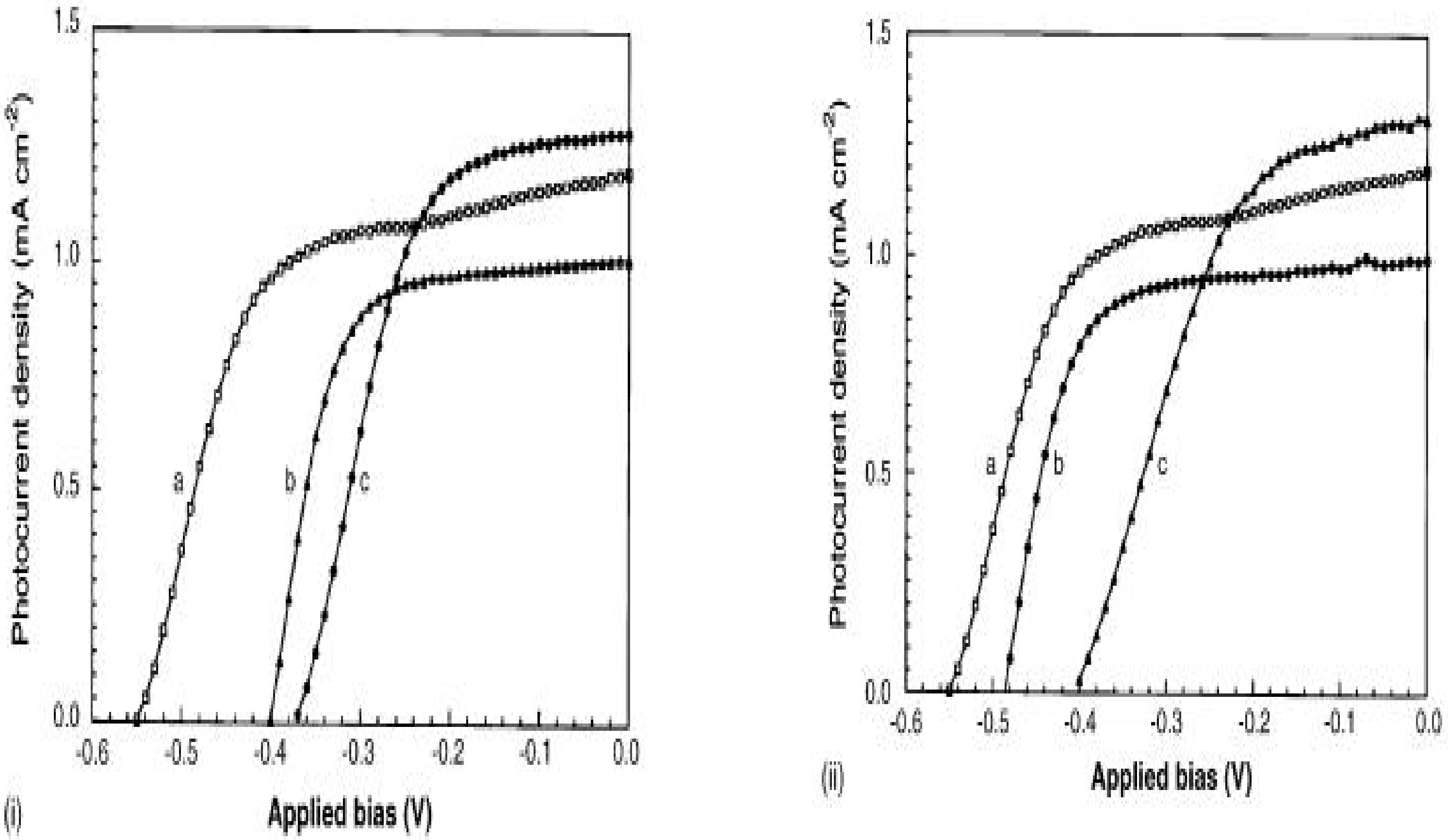


Fig. 6. n-GaAs photocurrent onset potential shifting by modification: (i) Metalloporphyrin-modified: (a) unmodified n-GaAs; (b) GaAs-MnP^{3+}; (c) GaAs-MnP^{5+}. (ii) Porphine-modified: (a) unmodified n-GaAs; (b) GaAs-H_2P^{2+}; (c) GaAs-H_2P^{4+}. (iii) Bipyridine-modified: (a) unmodified n-GaAs; (b) GaAs-bpy^{+}; (c) GaAs-bpy^{2+}. All measurements were conducted in aqueous Se^{2-}/Se_2^{2-}/KOH system.



Results of our earlier treatment

1) Shifts in Flat band potential
2) Shifts in open-circuit photovoltage V_{oc}
3) Enhanced photo-current

But Stability was not enhanced.
Monolayers pealed out.

Another Method: Treatment by Annealing

- n-GaAs and n-Si wafers were annealed between 400-900°C. Annealing enhanced photocurrent efficiency & surface topology.
- Rate of cooling also affected efficiency and surface topology as follows:

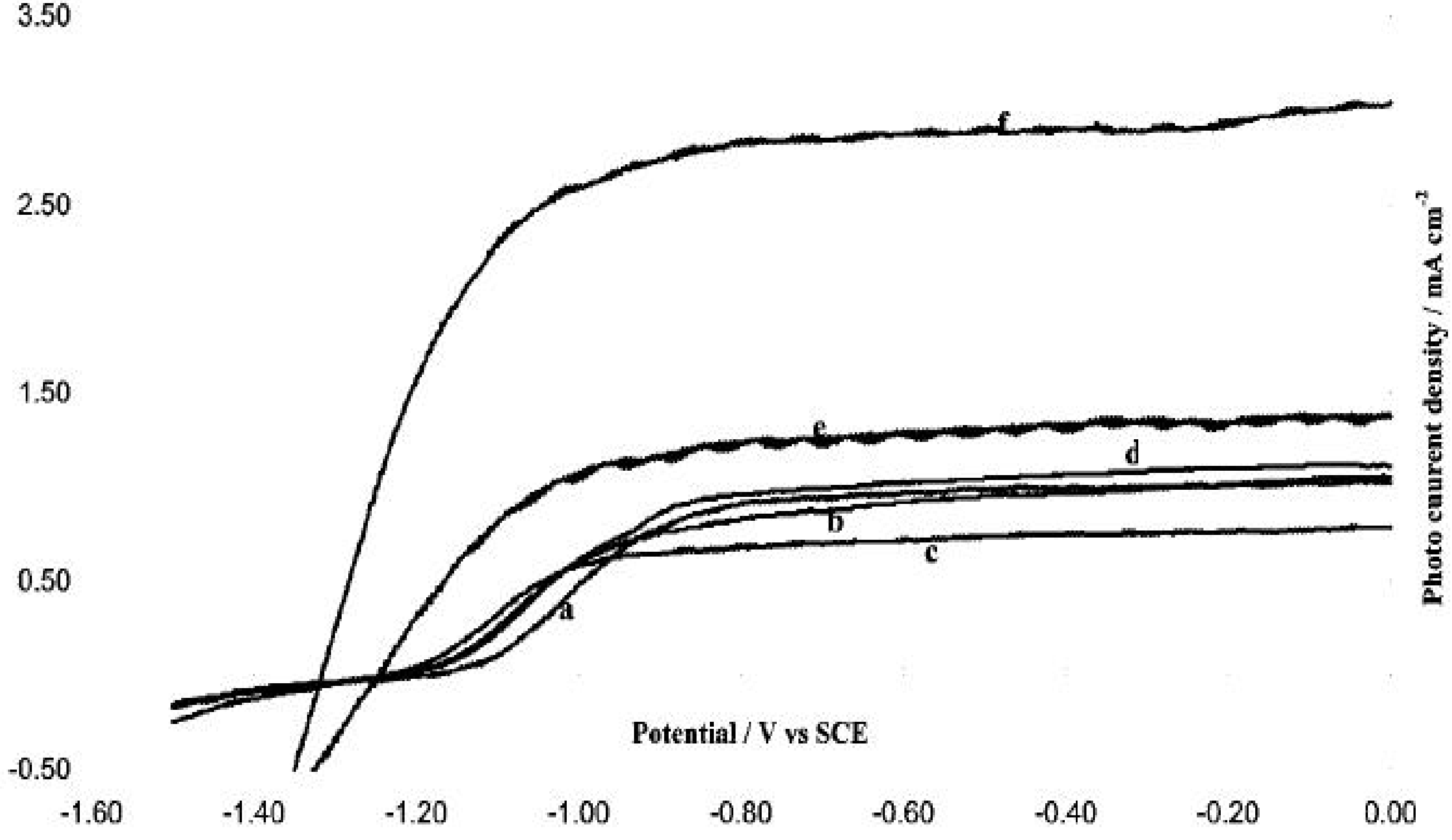
  -- From 600°C or below, slow cooling was better.

-- From 700°C and above, quenching was better

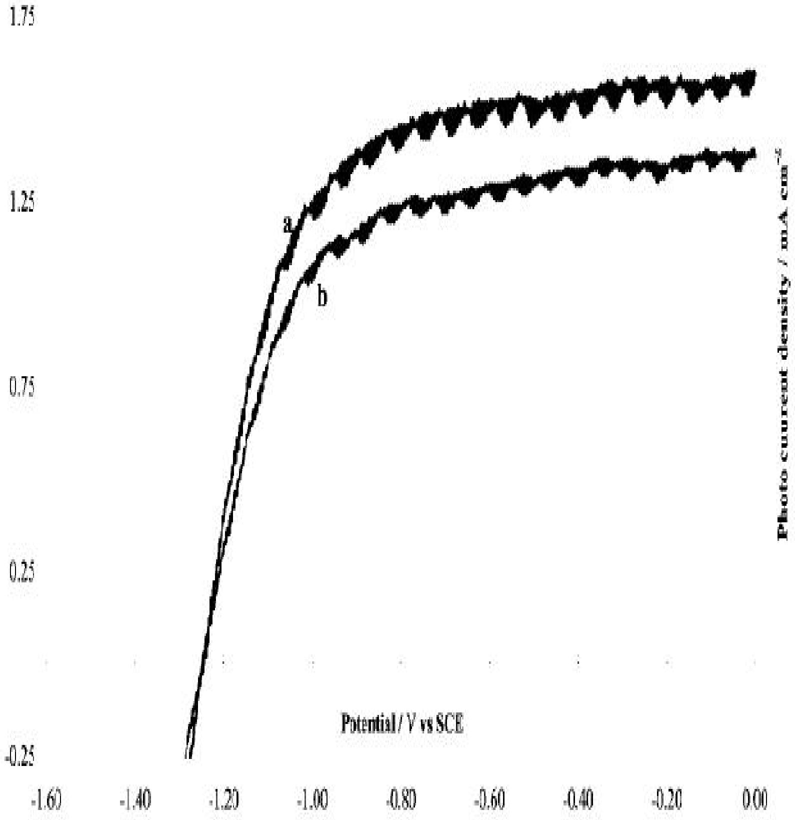
Effect of Annealing:

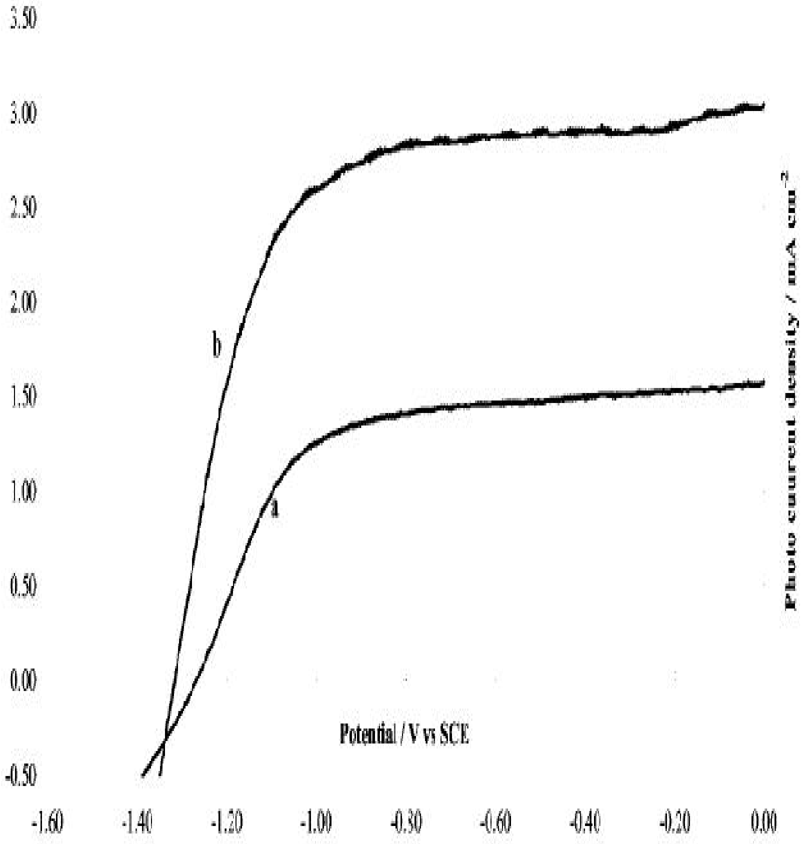
Photo J-V plots for n-GaAs untreated (a); and

quenched (b) from 400ºC (c) 500ºC, (d) 600ºC, (e) 700ºC, and (f) 800ºC



Effect of cooling rate: From 600ºC or below ; and from 700ºC and above. (a) slow cooling, (b) quenching





Effect on n-Si Crystal Surface: (1) untreated, (2) quenched from 400^{o}C, (3) slowly cooled from 400^{o}C

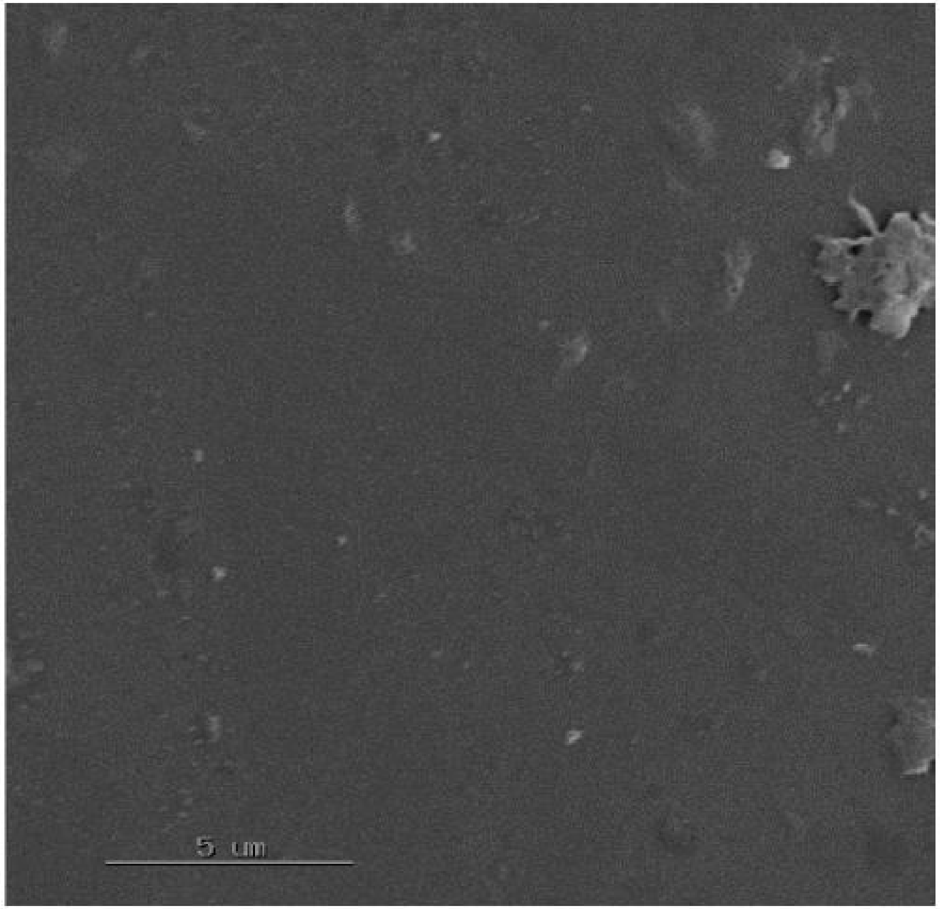


FIGURE 7 SEM image for untreated sample of *n*-Si with scale of 5 µm.

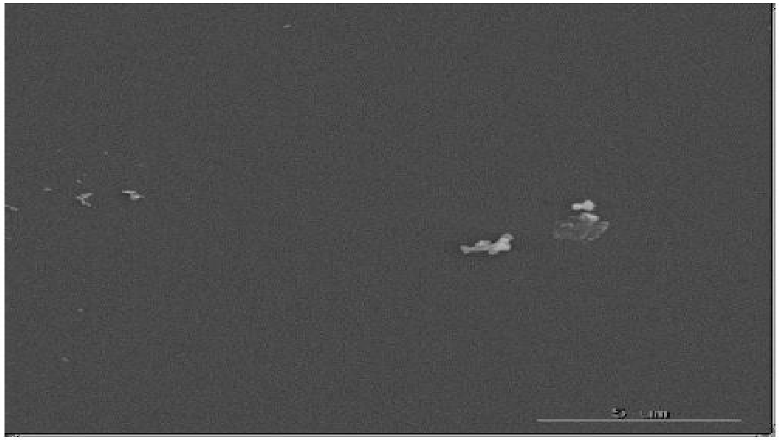


FIGURE 8 SEM for quenched sample of *n*-Si from 400 °C with scale of 5 µm

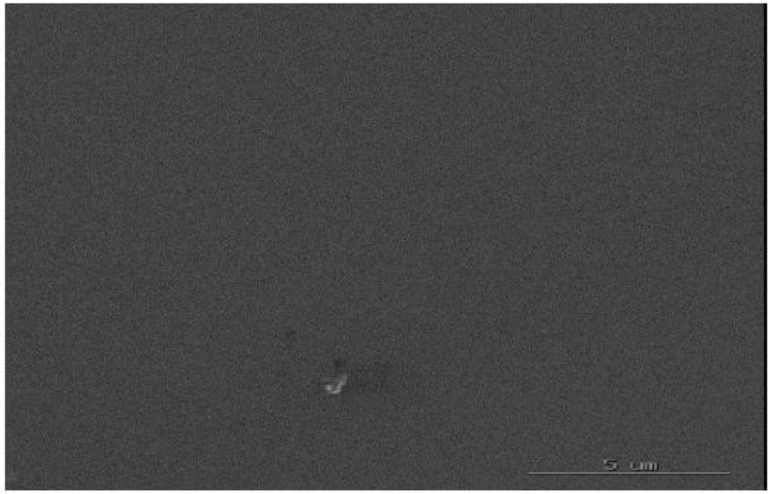


FIGURE 11 SEM for slowly cooled sample of *n*-Si from 400 °C with scale of 5 µm

Explanation:

- Annealing may exclude crystal imperfections (dislocations, ... etc)
- Slow cooling (from low temperatures) gives chance for defects to be repaired.
- Slow cooling (from high temperatures) may cause more defects.

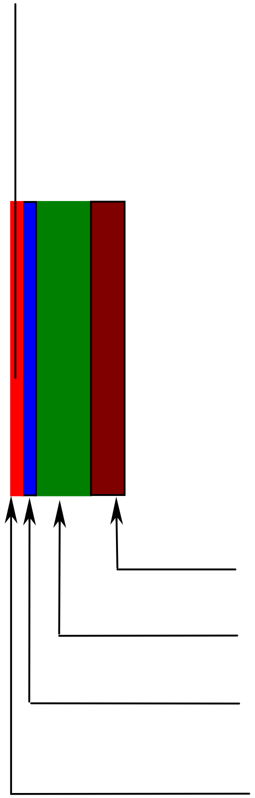
Our New Strategy was:

1) Enhancing Photocurrent
2) Enhancing Stability
3) Controlling the band edges

All these objectives to be achieved in one simple technique

New techniques

1) Metalloporphyrin /polysiloxane matrix (4 micron)
2) Preheating SC wafer
3) Method of cooling (quenching vs. slow cooling)



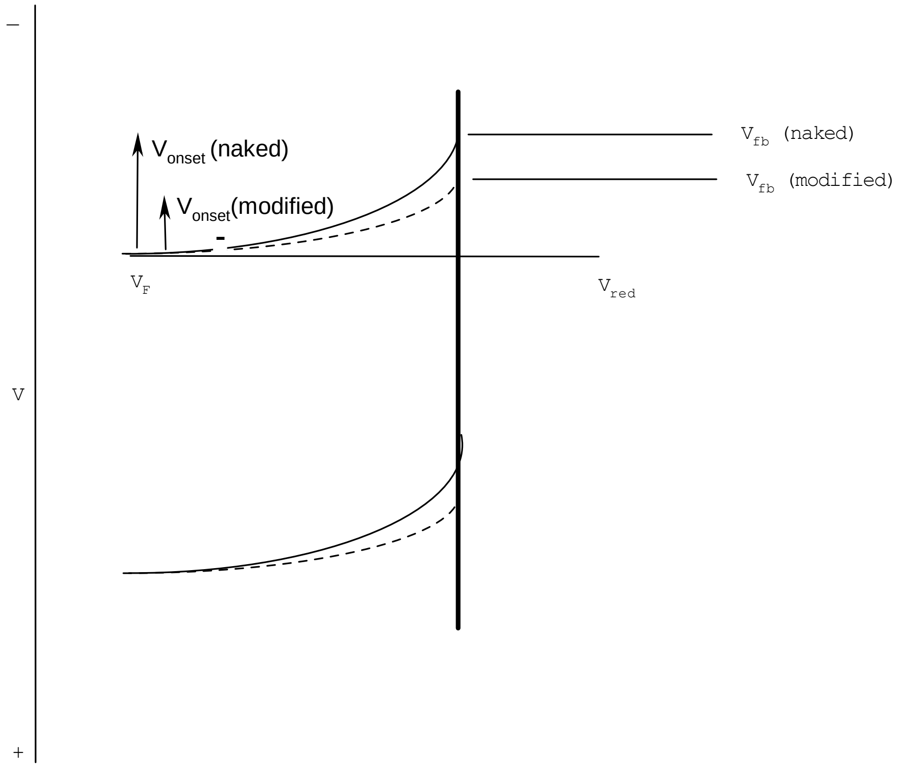
$\mathrm{Mn}^{\mathrm{II\ and\ III}}$(PyP) inside Polysiloxane

n-GaAs or n-Si

Ga-In eutectic contact

Copper Wiring

Effect of MnP Treatment on Dark Current vs. Potential Plots



Scheme 1

Combined treatment

- Preheating and MnP/Polysiloxane

Effect of combined treatment on photocurrent density: MnP/Polysiloxane and preheating (600^{o}C or lower)

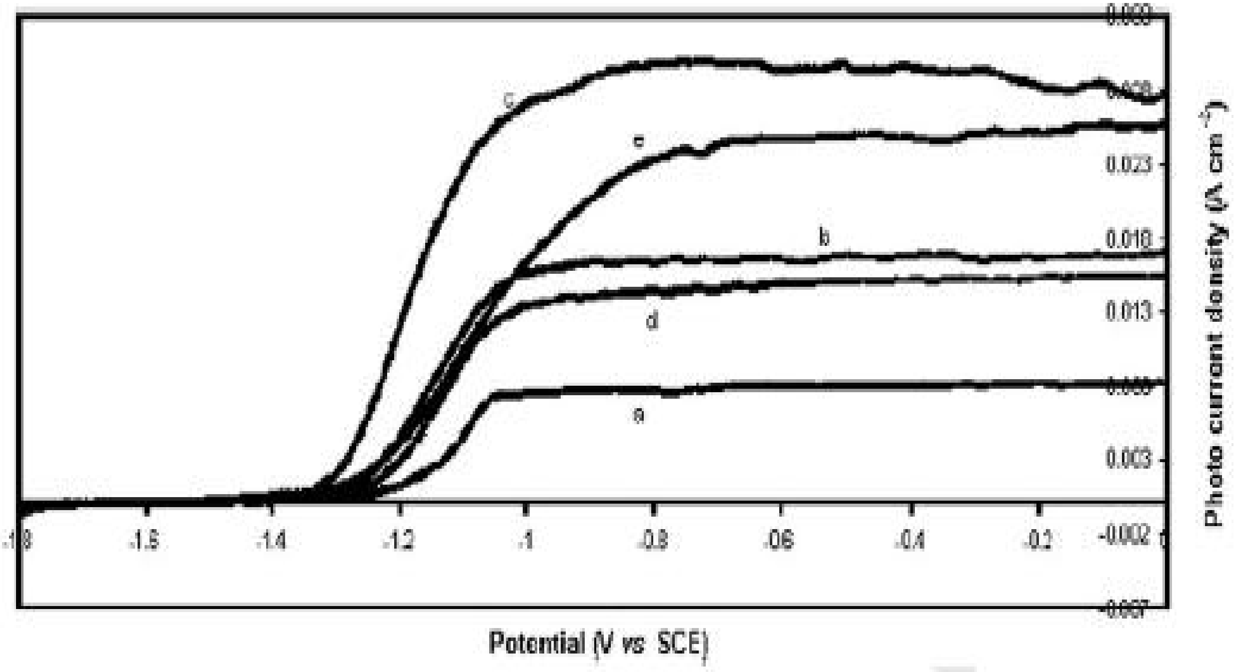


Fig. 3. Photo J–V plots for *n*-GaAs electrodes (a) untreated; and heated samples at 600 °C: (b) slowly cooled, (c) MnP-modified slowly cooled, (d) quenched, (e) MnP-modified quenched. All measurements were conducted in aqueous $K_2Se^{2-}/K_2Se_2^{2-}/KOH$ at 25 °C.

Effect of combined treatment on photocurrent density: MnP/Polysiloxane and preheating (800ºC)

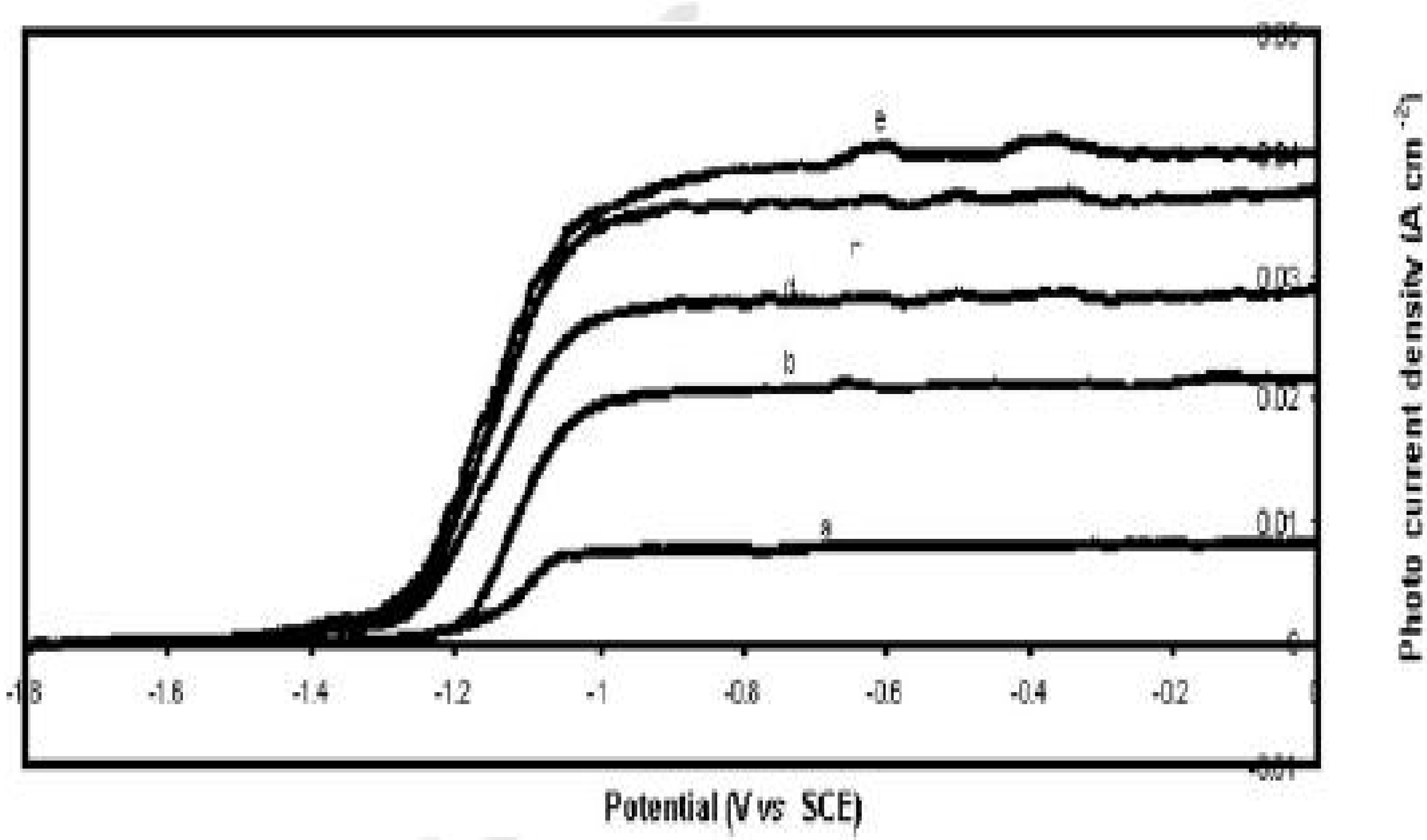


Fig. 5. Photo J–V plots for *n*-GaAs electrodes (a) untreated; and heated samples at 800 °C: (b) slowly cooled, (c) MnP-modified slowly cooled, (d) quenched, (e) MnP-modified quenched. All measurements were conducted in aqueous in K_2Se^{2-}/$K_2Se_3{}^{2-}$/KOH at 25 °C.

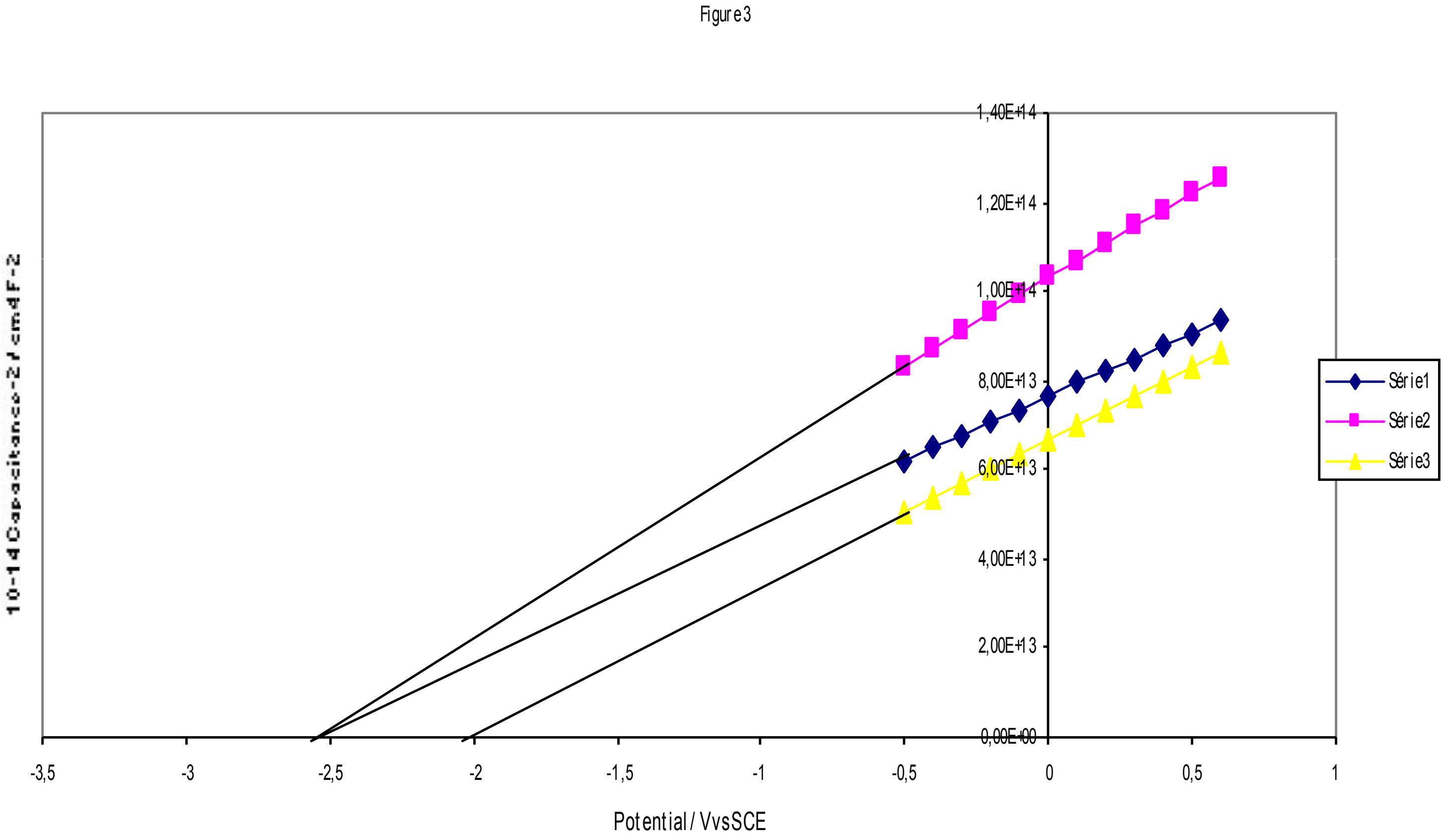
Combined preheating and MnP/Polysiloxane modification

- Gave better short circuit current
- Higher stability

Mott Schottky Plots (C^{-2} vs. Applied potential) for n-GaAs electrodes.

◊) untreated,) Polymer treated, Δ) MnP/polymer treated.

(Conditions as earlier). The Figure shows positive shifting in value of flat band potential



In Mott Schottky plots:
1/C2 is plotted vs. Applied potential
At 1/C2 = 0, Then Vfb can be obtained by extrapolation
The slope tells about doping density (DD) of SC

From the figure we knew about Vfb and DD

Effect of Treatment on Electrode Stability and efficiency.

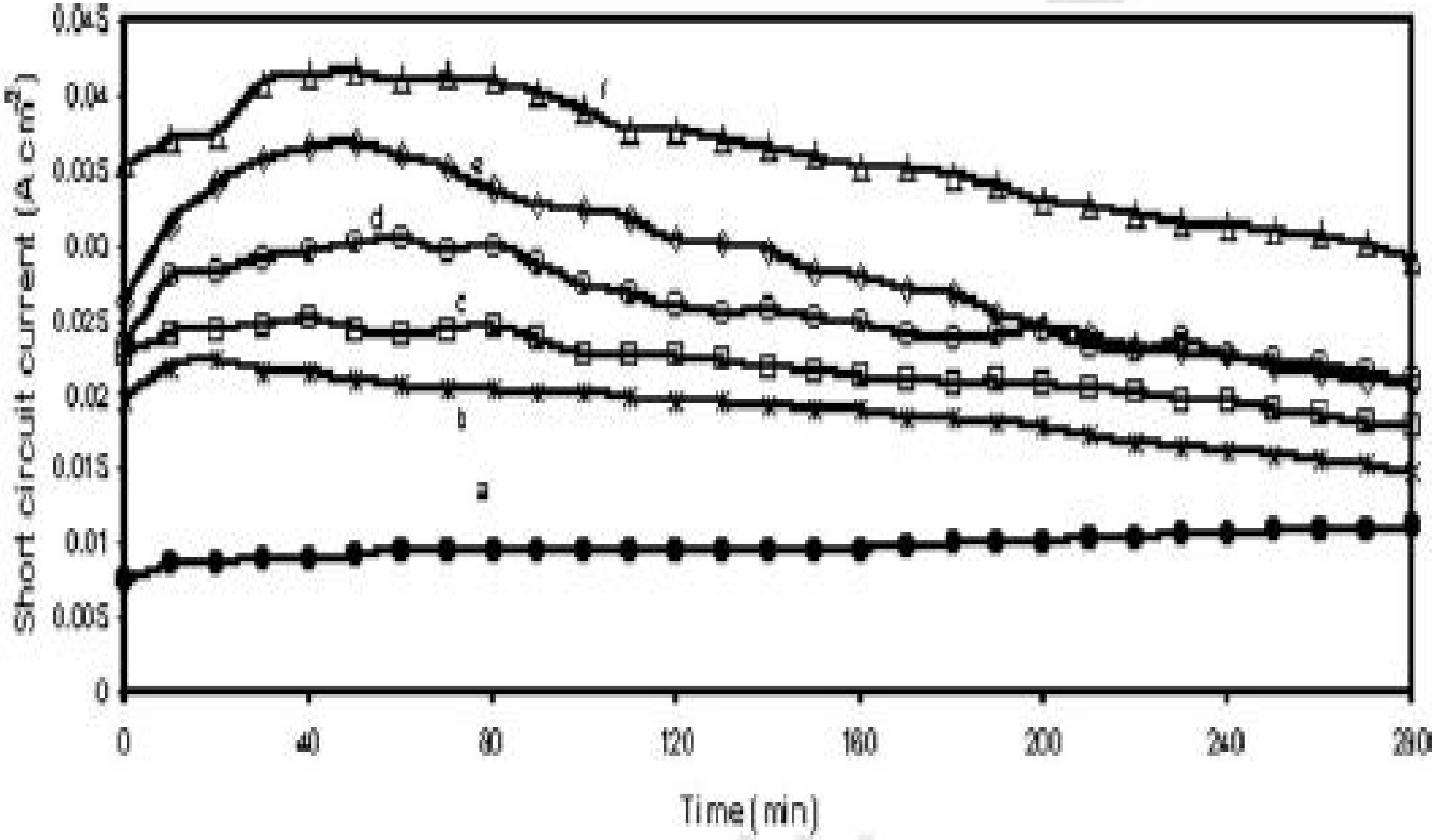
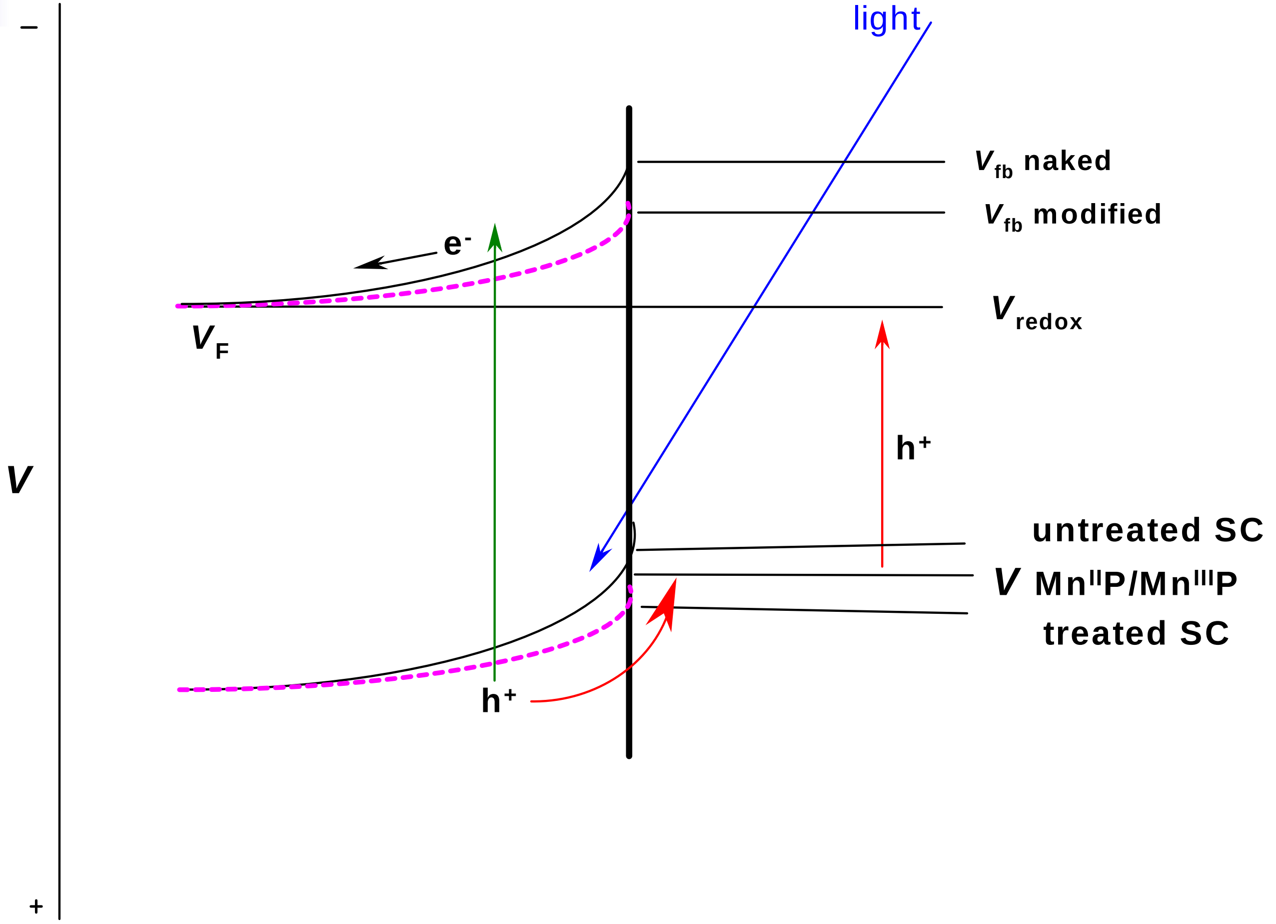


Fig. 8. Short circuit current vs time for *n*-GaAs electrodes (a) untreated (●); MnP-modified and quenched from: (b) 400 °C (∗), (c) 500 °C (□), (d) 600 °C (○), (e) 700 °C (◇) and (f) 800 °C (Δ). All measurements were conducted in aqueous in $K_2Se^{2-}/K_2Se_2^{2-}/KOH$ at 25 °C.

Mode of action of MnP in enhancing photocurrent and surface stability. Note the charge transfer catalytic behavior of the Mn^{II}P/Mn^{III}P couple.



Scheme II

Values of cell conversion efficiency for different n-GaAs electrodes.

[a] All measurements were conducted at 35ºC, earlier conditions. Cell maximum out put power was roughly calculated by multiplying the measured short circuit current ($I_{sc,}$ at 0.0 V) by the corresponding V value for the same electrode. Efficiency calculated by dividing the output power density by illumination intensity

Electrode [a]	Cell Efficiency % at different exposure times (min)					
	40	80	120	160	200	240
Naked n-GaAs	0.31	0.5	0.61	0.72	0.86	0.87
n-GaAs/Polymer	1.24	2.35	2.12	2.08	2.10	2.08
n-GaAs/MnP/Polymer	1.74	3.15	2.97	2.81	2.72	2.26

Conclusions for Part I

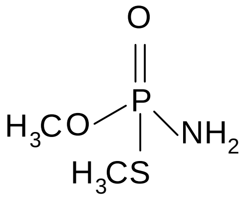
- MnP/Polysiloxane matrix increased Short-circuit current (up to 8 times) and enhanced stability
- Open-circuit potential was lowered (by up to 10%)
- Total cell output efficiency was enhanced.

Part II: Phtotelectrochemical Purification of Water

- Here radiation is used to degrade organic contaminants in water

Strategic Objectives

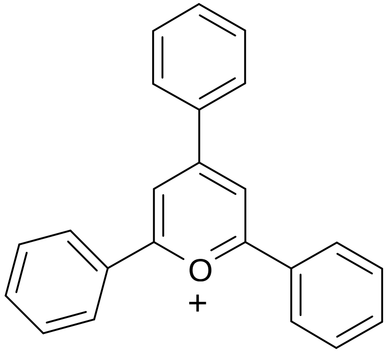
- Purify water from organic contaminants including Phenol, Benzoic acid and Tamaron
- Employ light for such purpose
- Tamaron (insecticide) is →



Technical Objectives

- Modify TiO_2 with dyes (TPPHS or metalloporphyrinato manganese(III) to give TiO_2/TPPHS or TiO_2/MnP systems.

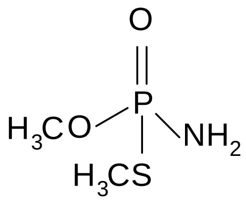
- Support TiO_2/dye onto activated carbon and use the AC/TiO_2/dye as catalyst
- TPPHS is: →



Wanted degradation processes

- Contaminant$_{(aq)}$ + $O_{2(g)}$ → $CO_{2(g)}$ + H_2O
- Contaminants here include →

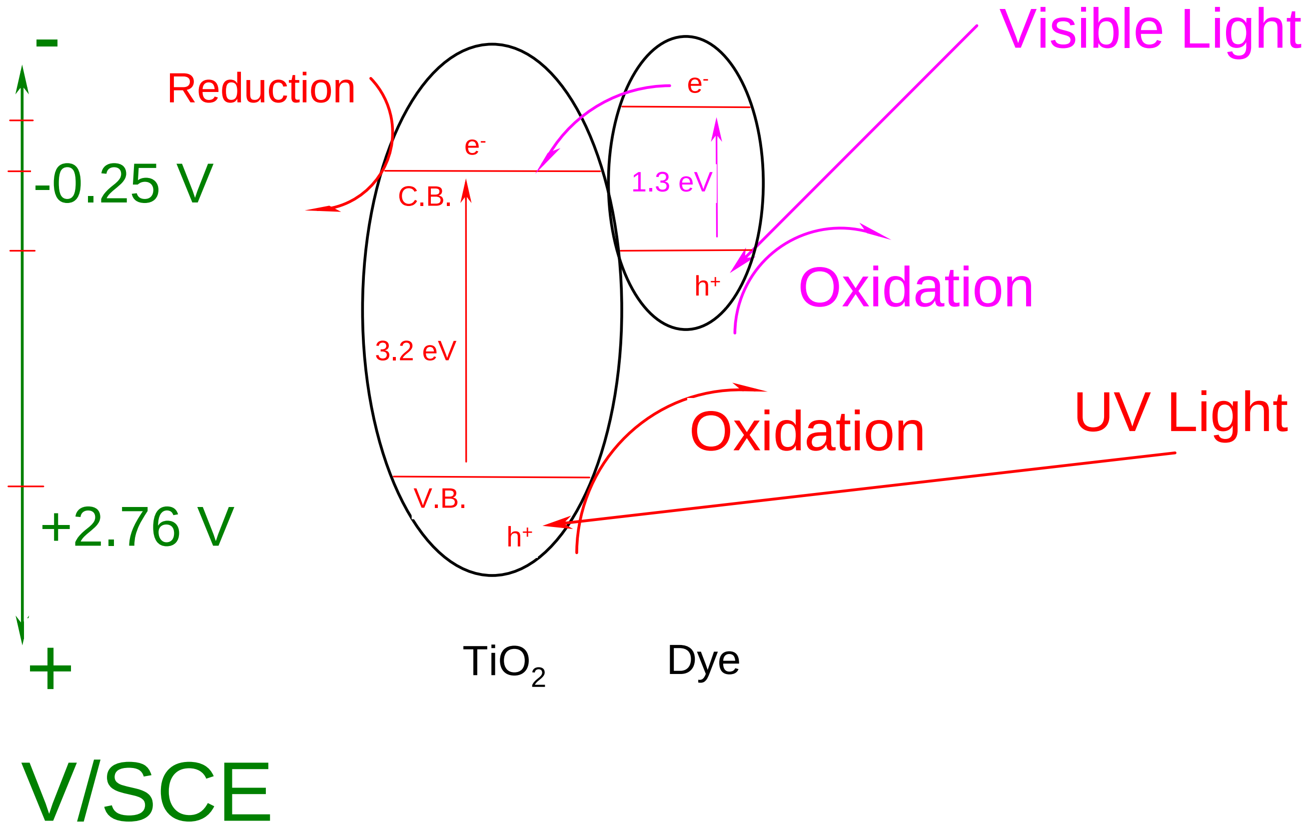
  Phenol , benzoic acid and Tamaron



Why Nano-crystals

- Nano-crystals 1-100 nm in diameter
- Much higher relative surface areas than mono-crystals
- Surface different, atoms not coordinatively saturated
- Higher surface activity than in large crystals

Theory of dye-sensitized TiO_2



Water purification with solar Light

- Light creates electron/hole pairs onto semiconductor
- Electron and holes separate
- Electrons reduce species: $O_2 + e \rightarrow 2O^{2-}$
- Holes oxidize species: Organic + $h^+ \rightarrow CO_2$

Thermodynamic Considerations

- To oxidize a contaminant, the holes must have a potential more positive (lower) the oxidation potential of that contaminant.
- The valence band for the Semiconductor must be lower than E_{ox} for contaminant.
- Some contaminants are stable, having Highly positive E_{ox}. (such as phenols, benzoic acid, chlorinated hydrocarbons).
- Some contaminants are not stable, having moderate E_{ox}. (such as heterocycles)

Energetics

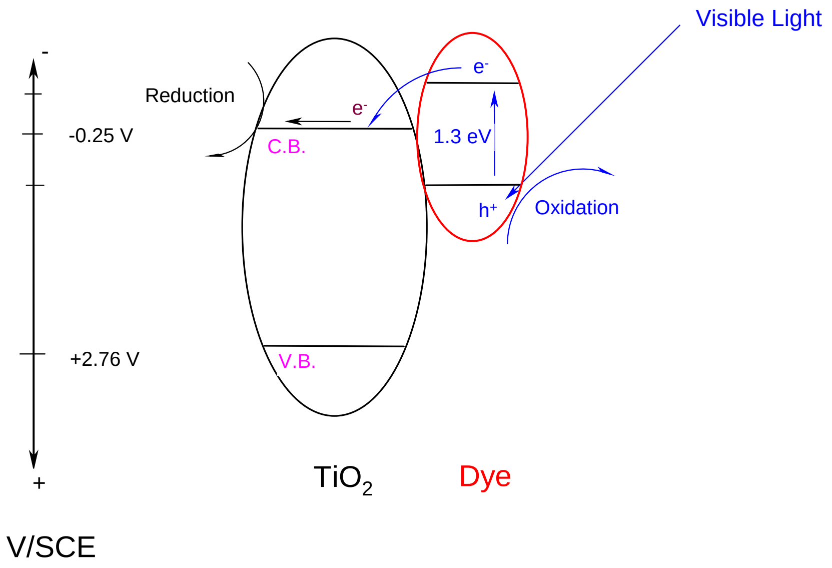
- Stable contaminants: demand highly positive potential holes: they demand TiO_2 with UV light.
- Unstable contaminants: demand moderate potentials
  Visible light is enough. Sensitized TiO_2 is enough.

SENSITIZATION

- Sensitization means creation of charge onto TiO_2 Conduction Band by visible light.
- Sensitization means allowing TiO_2 to function in the visible light
- The dye (sensitizer) is itself excited not the TiO_2.
- Sensitization involves the Visible region

Sensitization Mechanism

Good for low energy demanding processes



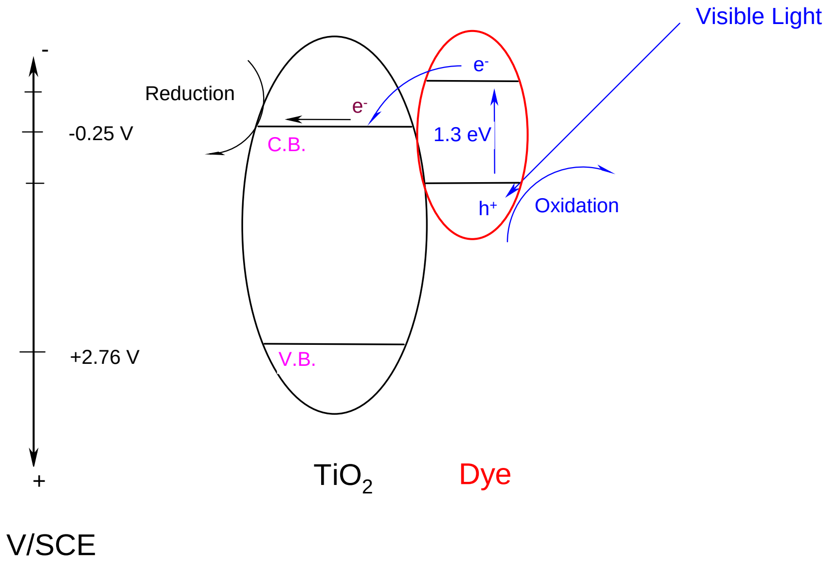
TiO_2 SENSITIZATION PROCESS:

*visible light is needed

*Low oxidizing power holes

Sensitization Mechanism

Good for low energy demanding processes

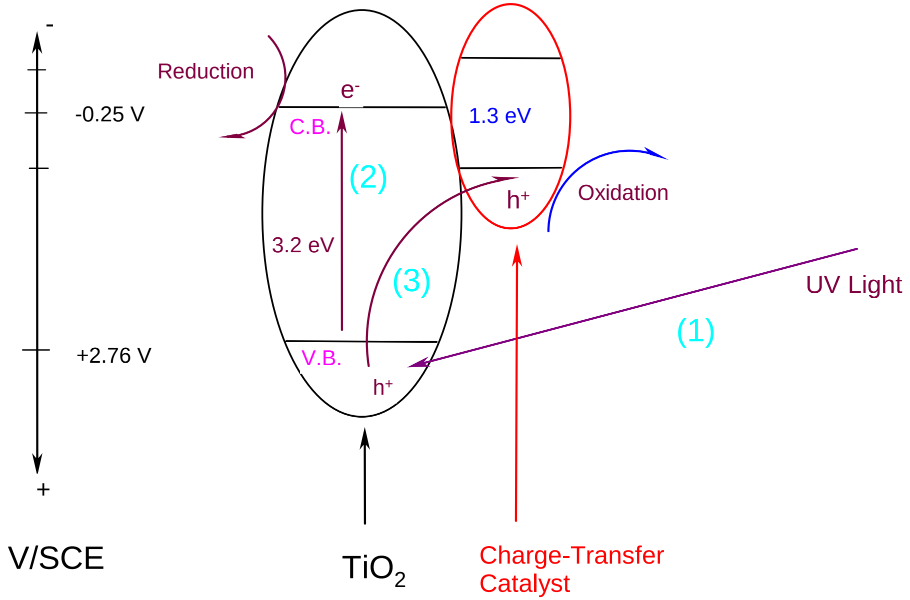


TiO_2 SENSITIZATION PROCESS:

*visible light is needed

*Low oxidizing power holes

Charge Transfer Catalysis
Good for high energy demanding processes



Charge Transfer Catalytic Effect:
* The dye is not excited itself
*The TiO_2 is itself oexcited with UV
*The holes are highly oxidizing, They oxidize contaminants
*The dye is a charge transfer catalyst only

Experimental Scheme

- Three round-bottomed flask (aqueous solution of contaminants)
- TiO_2 , dye (tripheny pyrilium ion), carbon, added
- UV, Hg(Xe), or visible lamp, W, complete with housing and power sources
- Sampling unit
- Stirring

Phenol Degradation Results

- Phenol did not degrade in the visible
- Phenol degraded only in the UV region
- TiO_2 only → not effective
- Dye only → not effective
- TiO_2/dye → effective in the UV This Indicates no sensitization process but charge transfer catalytic process for phenol. See Tables and results

Table 1: Turnover Number values for different catalytic systems in Phenol degradation

Catalyst	TiO_2 amount g	TPPHS amount g (mol)	Turnover number after 120 min. (reacted PhOH moles /dye moles
Naked TiO_2	???	0.00	33*
Dye only	0.00	0.006 ($1.476X10^{-5}$)	27
TiO_2/TPPHS	0.5	0.01 ($2.46X10^{-5}$)	163
	0.5	0.005 ($1.23X10^{-5}$)	129
	1.0	0.006 ($1.476X10^{-5}$)	149
	0.5??	0.006 ($1.467X10^{-5}$)	270
	0.5	0.003 g ($0.738X10^{-5}$ mol)	176
AC/TiO_2/TPPHS	0.5	0.006 ($1.476X10^{-5}$)	372
	0.5	0.003 ($0.738X10^{-5}$)	
	0.5	0.012 ($2.952X10^{-5}$)	169???
	0.5	0.01	677
	0.5	0.003 ($0.738X10^{-5}$)	580

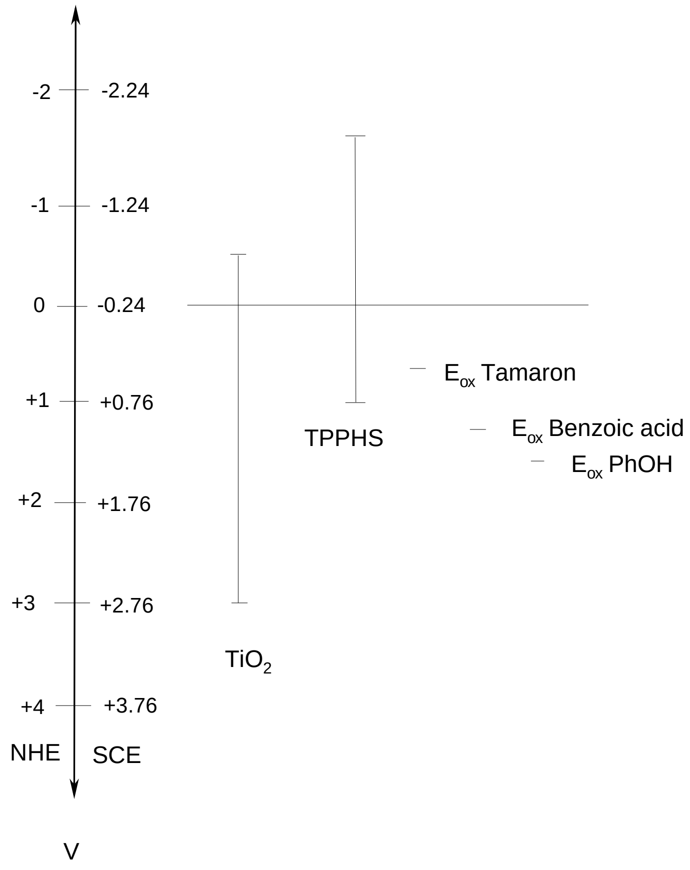
Benzoic Acid Degradation Results

- Degraded in UV not in Visible
- TiO_2 low effect
- Dye low effect
- TiO_2/Dye high effect in the UV, indicating no sensitization, but Charge transfer catalysis

Tamaron Degradation Results

- Tamaron degraded in the visible
- TiO_2 alone did not work efficitively
- Dye alone not effective
- TiO_2/Dye effective for Tamaron (in the visible) and in the UV as well.
- This indicates sensitization (Visible) & charge transfer catalysis (UV)

Semiconductor band energetics and degradation demands



-2 -2.24

-1 -1.24

0 -0.24

+1 +0.76

+2 +1.76

+3 +2.76

+4 +3.76

NHE SCE

V

TiO$_2$

TPPHS

E$_{ox}$ Tamaron

E$_{ox}$ Benzoic acid

E$_{ox}$ PhOH

Activated Carbon Results

- AC enhanced the degradation process in phenol, benzoic acid and Tamaron.
- AC possibly adsorbs the contaminant molecules.
- It brings them into close proximity with the catalytic sites.

Conclusions for Part II

- Phenol (a stable contaminant) demands UV in case of TiO_2/Dye with or without AC
- Benzoic acid demands UV, in case of TiO_2/Dye (with or without AC)
- Tamaron demands only Visible, in case of TiO_2/Dye (with or without AC)
- AC enhances the catalytic efficiency in each time
- Phenol and benzoic acid degradation goes through a charge transfer mechanism
- Tamaron degradation goes through a sensitization process.

Future Perspectives

- Use thin films of Support/TiO_2/Dye to maximize exposure to light.
- Use continuous flow rate reactors.
- Use safe dyes (natural and plant dyes)
- Use other SC materials.

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