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:

Strategic Objectives

- Utilize solar energy in large scale, economically 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: Principle, advantages and disadvantages

Conducting back contact

thin conducting transparent film

light to electricity in p-n junctions
Photoelectrochemical (PEC) Devices: Principles, advantages and disadvantages

Photoelectrochemical cell

SC electrode

Counter electrode (platinum)

light

e-

redox couple/electrolyte/liquid
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

\[ \text{Scheme I} \]

\[ \begin{align*}
\text{untreated} & \quad V_f \\
\text{treated} & \quad V_f
\end{align*} \]

\[ \text{V_{redox}} \]

\[ \begin{align*}
2\text{H}_2\text{O} + 4\text{e}^- & \rightarrow 2\text{H}_2\text{(g)} \\
2\text{H}_2\text{O} + 4\text{h}^+ & \rightarrow \text{O}_2
\end{align*} \]
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

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\textsubscript{4}(aq) (0.1 M), no added redox couples. (a) Unmodified n-GaAs and (b) GaAs-MnP\textsuperscript{3+}. 

(a) $C^{-2}$ vs. $\text{Potential (V) vs. SCE}$

(b) $C^{-2}$ vs. $\text{Potential (V) vs. SCE}$
Fig. 6. n-GaAs photocurrent onset potential shifting by modification: (i) Metalloporphyrin-modified: (a) unmodified n-GaAs; (b) GaAs-MnP$_{3}^{3+}$; (c) GaAs-MnP$_{5}^{5+}$. (ii) Porphine-modified: (a) unmodified n-GaAs; (b) GaAs-H$_{2}$P$_{2}^{2+}$; (c) GaAs-H$_{2}$P$_{4}^{4+}$. (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.

(i) Photocurrent density (mA cm$^{-2}$) vs. Applied bias (V)

(ii) Photocurrent density (mA cm$^{-2}$) vs. Applied bias (V)
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 peeled 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 400°C (c) 500°C, (d) 600°C, (e) 700°C, and (f) 800°C.
Effect of cooling rate: From 600°C or below; and from 700°C and above. (a) slow cooling, (b) quenching.
Effect on n-Si Crystal Surface: (1) untreated, (2) quenched from 400°C, (3) slowly cooled from 400°C
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)
Effect of MnP Treatment on Dark Current vs. Potential Plots

Scheme 1

- $V_{\text{onset}}$ (naked)
- $V_{\text{onset}}$ (modified)
- $V_{\text{fb}}$ (naked)
- $V_{\text{fb}}$ (modified)

$V_f$ $V_{\text{red}}$
Combined treatment

- Preheating and MnP/Polysiloxane
Effect of combined treatment on photocurrent density: MnP/Polysiloxane and preheating (600°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 $K_2Se^3-/K_2Se_2^{2-}/KOH$ at 25°C.
Effect of combined treatment on photocurrent density: MnP/Polysiloxane and preheating (800°C)

Fig. 5. Photo J–V plot 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 K₂Se⁺⁻/K₂Se₂⁻⁻/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, △) 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 K₂Se²⁻/K₂Se₂⁻/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. All measurements were conducted at 35°C, earlier conditions. Cell maximum output 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.

<table>
<thead>
<tr>
<th>Electrode $^a$</th>
<th>Cell Efficiency % at different exposure times (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>40</td>
</tr>
<tr>
<td>Naked n-GaAs</td>
<td>0.31</td>
</tr>
<tr>
<td>n-GaAs/Polymer</td>
<td>1.24</td>
</tr>
<tr>
<td>n-GaAs/MnP/Polymer</td>
<td>1.74</td>
</tr>
</tbody>
</table>
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: Photoradiochemical 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: →

![Chemical Structure of TPPHS](image_url)
Wanted degradation processes

- Contaminant_{(aq)} + O_2(g) \rightarrow CO_2(g) + H_2O
- Contaminants here include → Phenol, benzoic acid and Tamaron
Why Nano-cryystals

- 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 TiO₂

- Visible Light
- UV Light

V/SCE

+2.76 V

-0.25 V

Reduction

Oxidation

V.B.

C.B.

TiO₂

Dye

3.2 eV

1.3 eV
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.
**TiO$_2$ Sensitization Mechanism**

Good for low energy demanding processes

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**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 excited with UV
* The holes are highly oxidizing, they oxidize contaminants
* The dye is a charge transfer catalyst only

\[
\begin{align*}
\text{V.B.} &\to \text{C.B.} \\
\text{h}^+ &\to \text{e}^- \quad \text{Reduction} \\
1.3 \text{ eV} &\to 3.2 \text{ eV} \\
+2.76 \text{ V} &\to -0.25 \text{ V} \\
\text{UV Light} &\to \text{Charge-Transfer Catalyst}
\end{align*}
\]
Experimental Scheme

- Three round-bottomed flask (aqueous solution of contaminants)
- TiO\(_2\), dye (triphenyl 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 region.
- Phenol degraded only in the UV region.
- TiO$_2$ only $\rightarrow$ not effective.
- Dye only $\rightarrow$ not effective.
- TiO$_2$/dye $\rightarrow$ 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**

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>TiO₂ amount g</th>
<th>TPPHS amount g (mol)</th>
<th>Turnover number after 120 min. (reacted PhOH moles /dye moles)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naked TiO₂</td>
<td>???</td>
<td>0.00</td>
<td>33*</td>
</tr>
<tr>
<td>Dye only</td>
<td>0.00</td>
<td>0.006 (1.476X10⁻⁵)</td>
<td>27</td>
</tr>
<tr>
<td>TiO₂/TPPHS</td>
<td>0.5</td>
<td>0.01 (2.46X10⁻⁵)</td>
<td>163</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.005 (1.23X10⁻⁵)</td>
<td>129</td>
</tr>
<tr>
<td></td>
<td>1.0</td>
<td>0.006 (1.476X10⁻⁵)</td>
<td>149</td>
</tr>
<tr>
<td></td>
<td>0.5???</td>
<td>0.006 (1.467X10⁻⁵)</td>
<td>270</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.003 g (0.738X10⁻⁵ mol)</td>
<td>176</td>
</tr>
<tr>
<td>AC/TiO₂/TPPHS</td>
<td>0.5</td>
<td>0.006 (1.476X10⁻⁵)</td>
<td>372</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.003 (0.738X10⁻⁵)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.012 (2.952X10⁻⁵)</td>
<td>169??</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.01</td>
<td>677</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>0.003 (0.738X10⁻⁵)</td>
<td>580</td>
</tr>
</tbody>
</table>
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 effectively
- 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
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.
Acknowledgement

- An-Najah N., University laboratories.
- ICMCB, Bordeaux, France for SEM and TGA study.
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