

Sustainable Solar Energy Technologies & Job Opportunities

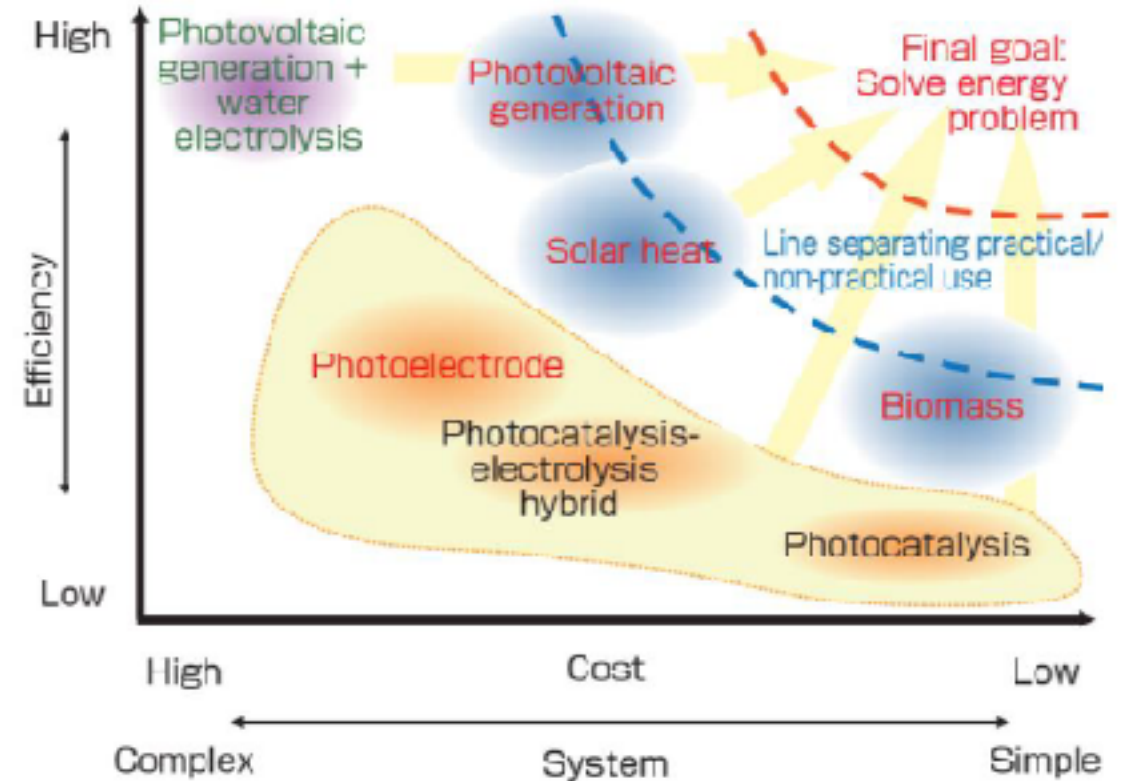


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5. Solar to fuel technologies: Artificial photosynthesis, Photoelectrochemical cells, Photoelectrode interface, solar energy conversion at solid/liquid interface, photoelectrode criteria, photoelectrochemical solar cell, PE fuel cell, DSSC, solar energy conversion in biosystems, Artificial photoelectrosynthesis, solar fuels, biomimics, Carbon dioxide reduction, solar chargeable energy storage systems, Challenges in commercialization

Artificial photosynthesis

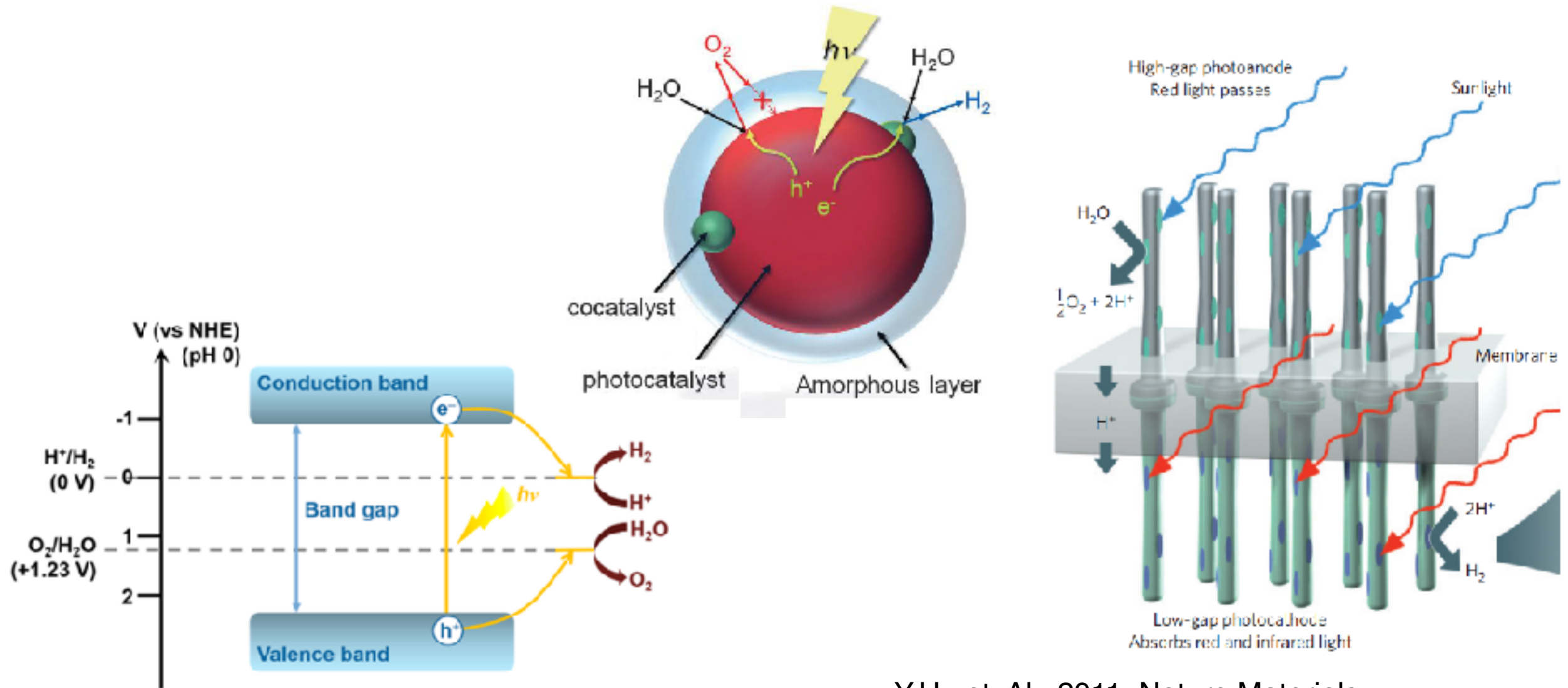
- Natural process of **photosynthesis** fix the solar energy chemical bonds (biomass)
- Light conversion efficiency is less even for natural photosynthesis process (3 to 5 %)
- Photovoltaic devices are with higher efficiency (lab scale 47%), but not cost effective and more complex preparation
- Photoelectrosynthesis or artificial photosynthesis are lower cost compared to photovoltaic devices but with lower conversion efficiency
- Here the useful small chemical molecules are prepared using photoelectrodes in photoelectrochemical cells



Artificial photosynthesis

- Natural process of photosynthesis fix the solar energy chemical bonds
- Photo - Electrochemical cells are used to convert solar energy at the electrode/electrolyte interface
- Here the light energy is converted to chemical energy
- Small molecules like Hydrogen, methane, Ethane, ethanol, ethene can be produced
- Efficiency is less compared to photovoltaic cell but use cheaper and polycrystalline photo active materials
- The photoelectrode materials should be stable in electrolyte

Photocatalyst – Photoelectrode comparison



Y.Hu et. Al., 2011, Nature Materials

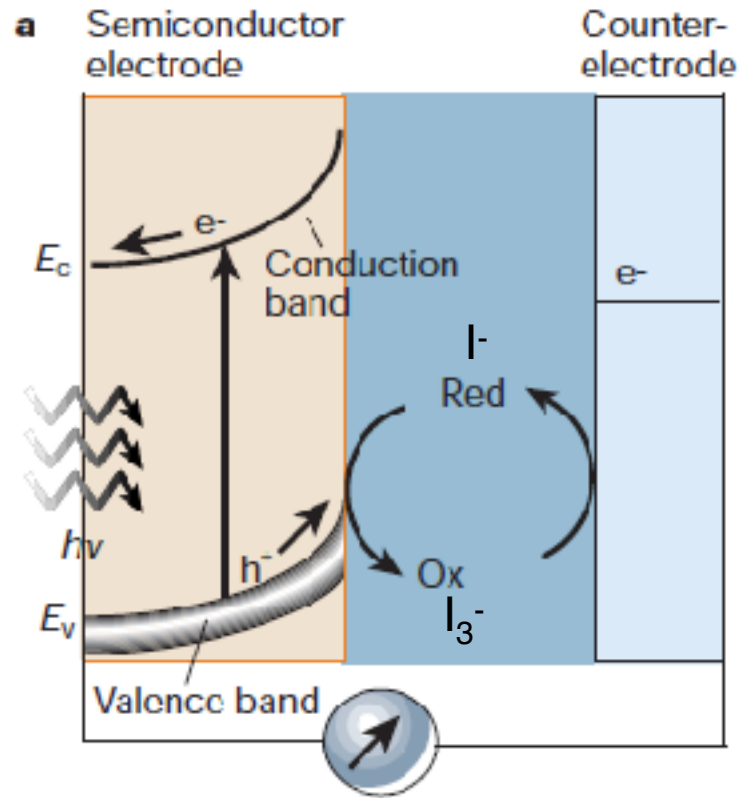
Photocatalyst vs photoelectrochemical cell

- Photoactive materials absorb light to create holes(valence band) and electrons (Conduction band)
- In photocatalyst both oxidation (VB) and reduction (CB) occurs from respective bands
- Both oxygen and hydrogen evolved simultaneously on photocatalysts
- Photoelectrochemical cell will separate directly the hydrogen and oxygen there is no need of further separation – reduce the energy and cost.
- Need of n-type photoanode materials for oxidation, p-type photocathode materials for reduction
- Membrane allows the separation between anodic and cathodic sides

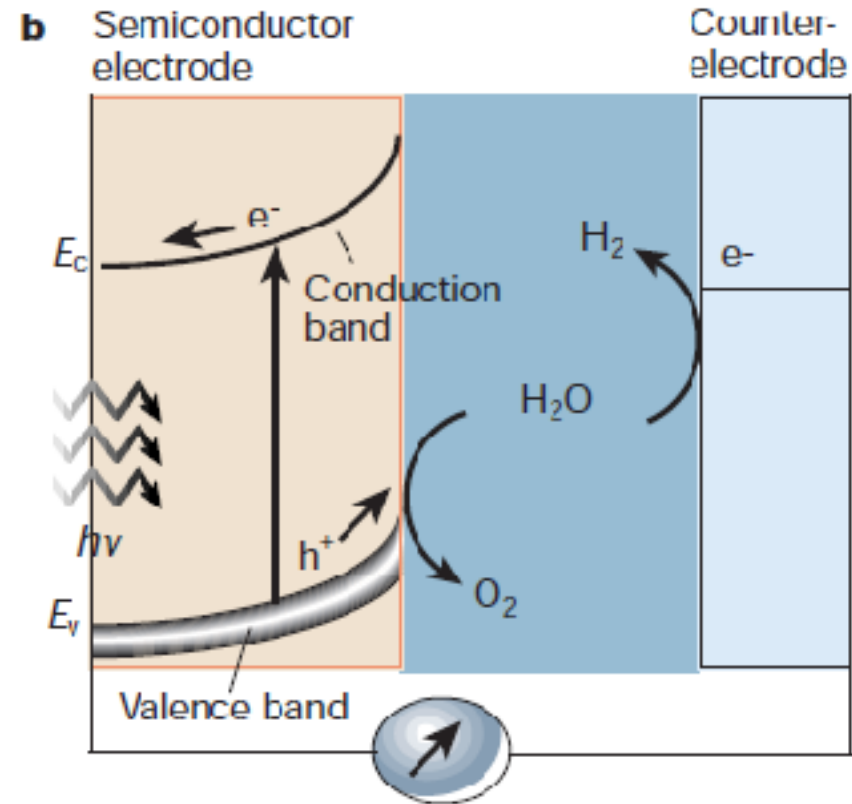
Photoelectrode characteristics

- Photoelectrode materials should absorb visible light to create holes(valence band) and electrons (Conduction band)
- In photoelectrode should prefer oxidation (VB) in n-type semiconductor and reduction (CB) in p-type semiconductor
- Should separate the photogenerated charges and avoid recombination
- Electrode material should be thin film with high absorptivity coefficient
- It should be stable without corrosion or degradation in aqueous medium
- Photoelectrochemical cell the electrode band should favour preferred process
- Should easily separate charges at the interface

Photoelectrochemical cells

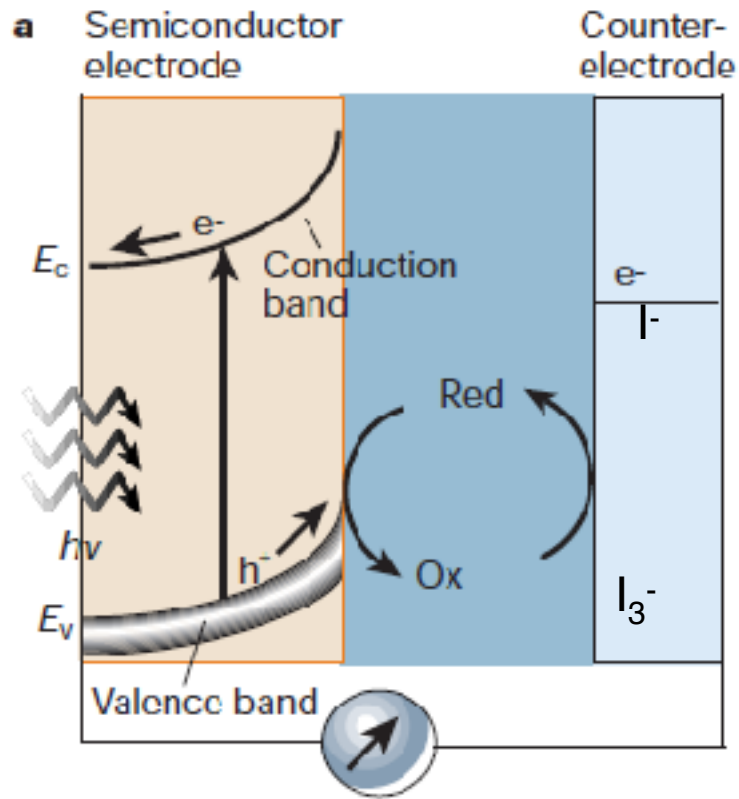


a. Photoelectrochemical regenerative solar cell



b. Photoelectrochemical solar to fuel cell

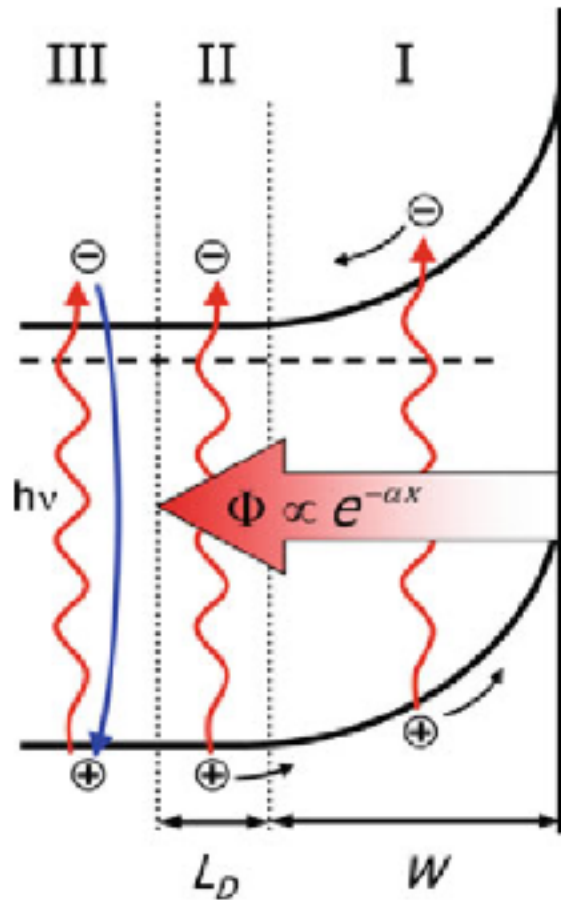
Photoelectrochemical solar cells



- Photoelectrode absorb light and undergo band bending at electrode/electrolyte interface
- n-type photoanode allow oxidation
- p-type photocathode allow reduction
- Use of redox couple (e.g., I^-/I_3^- , S_2^{2-}/S_2^{2-}) to maintain cell equilibrium and tap the photoexcited charges at the interface.
- Regenerative cell due to cell equilibrium
- Cheap and stable photoelectrodes, n-TiO₂, n-Fe₂O₃, p-Cu₂O, p-CuFeO₂)

a. Photoelectrochemical regenerative solar cell

Light absorption and photoprocess in n-type SC



Region I:

- Absorption
- Charge separation
- Field-assisted transport (drift)

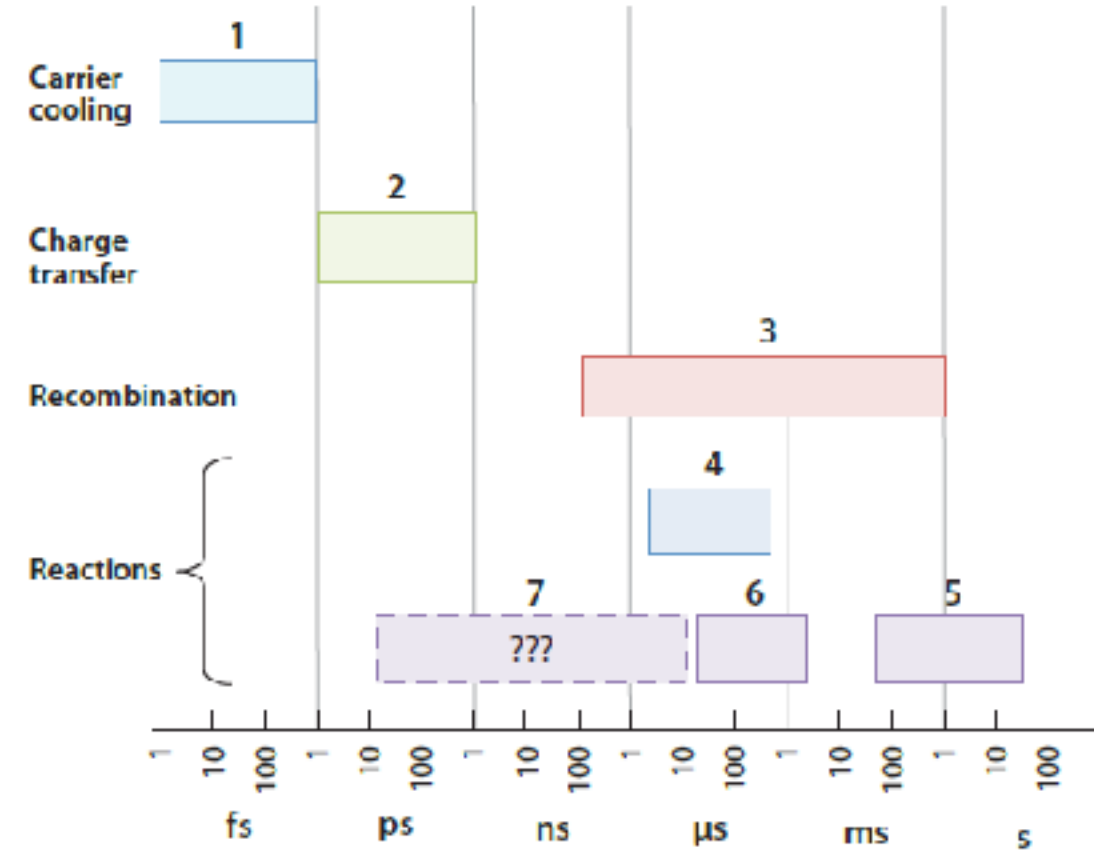
Region II:

- Absorption
- Transport by diffusion
- Holes are able to reach region I before recombining

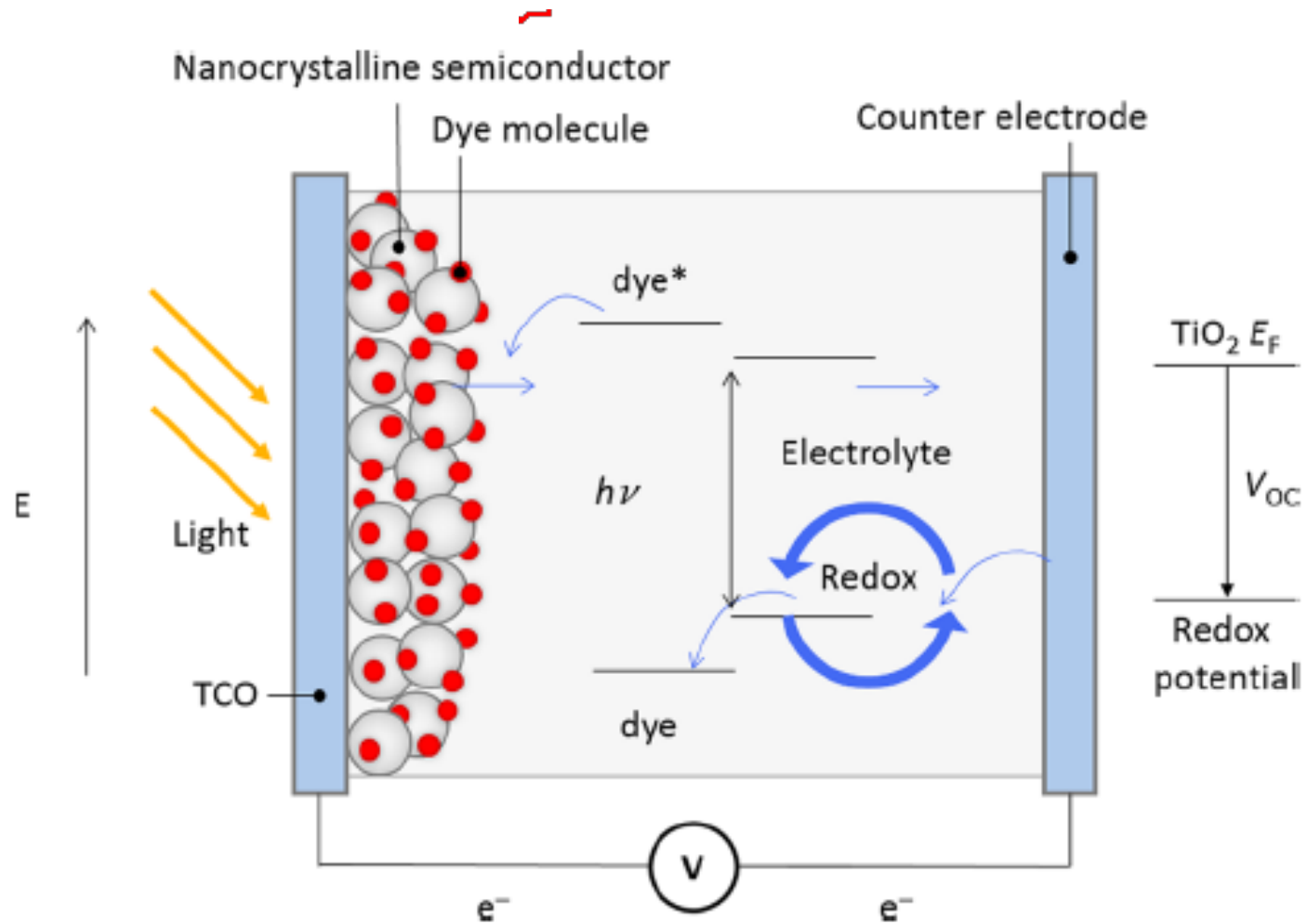
Region III:

- Absorption + recombination

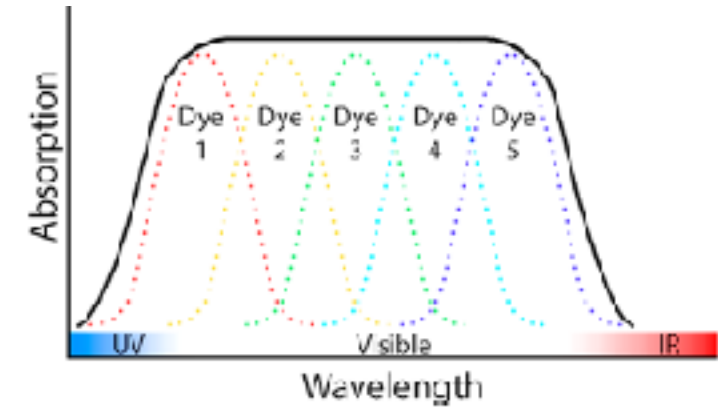
Optimal film thickness: $d \approx \alpha^{-1} \approx W + L_D$



Dye sensitized solar cell (DSSC) – Graetzel cell



Visible absorption by dyes



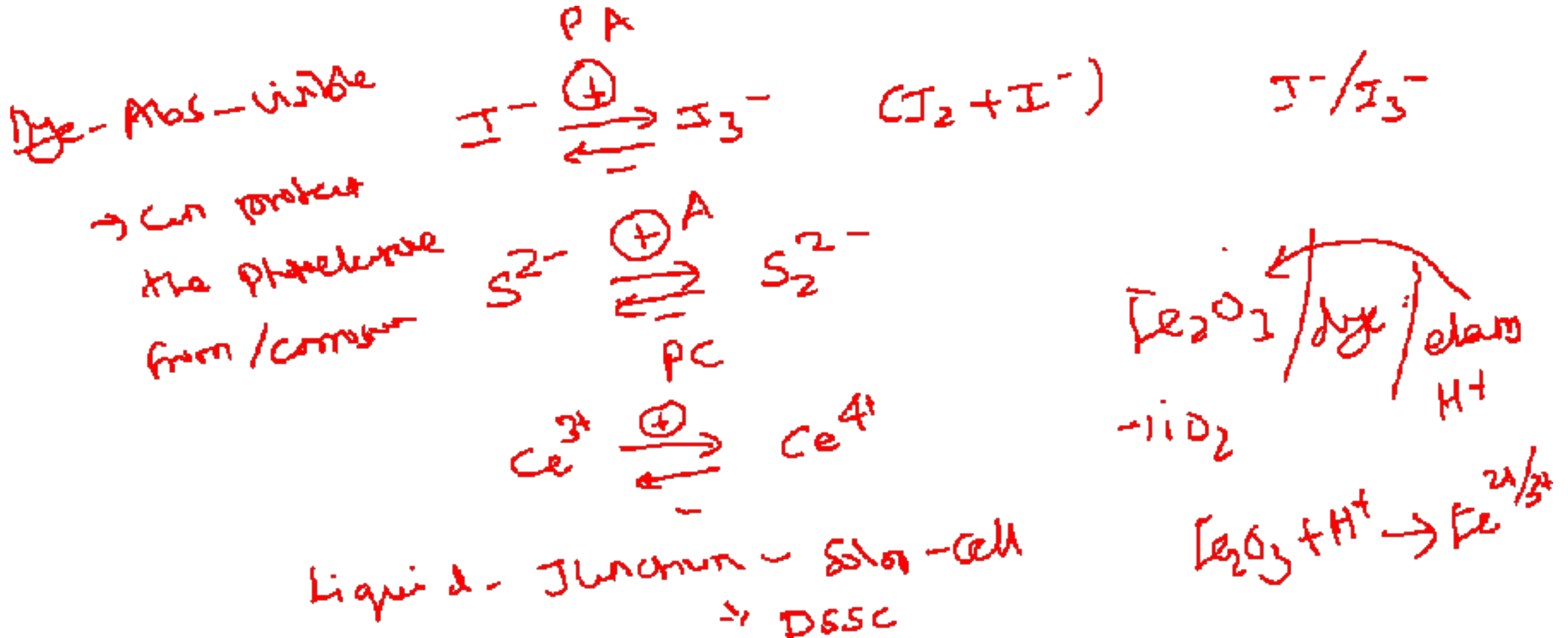
- Dye for sensitization and broad spectrum light absorption
- Works on the principle of redox shuttling to generate Reversible solar cell
- Can enhance the charge separation and injection
- Protect the underlying inorganic semiconductor photoelectrode

Photoelectrochemical solar cells

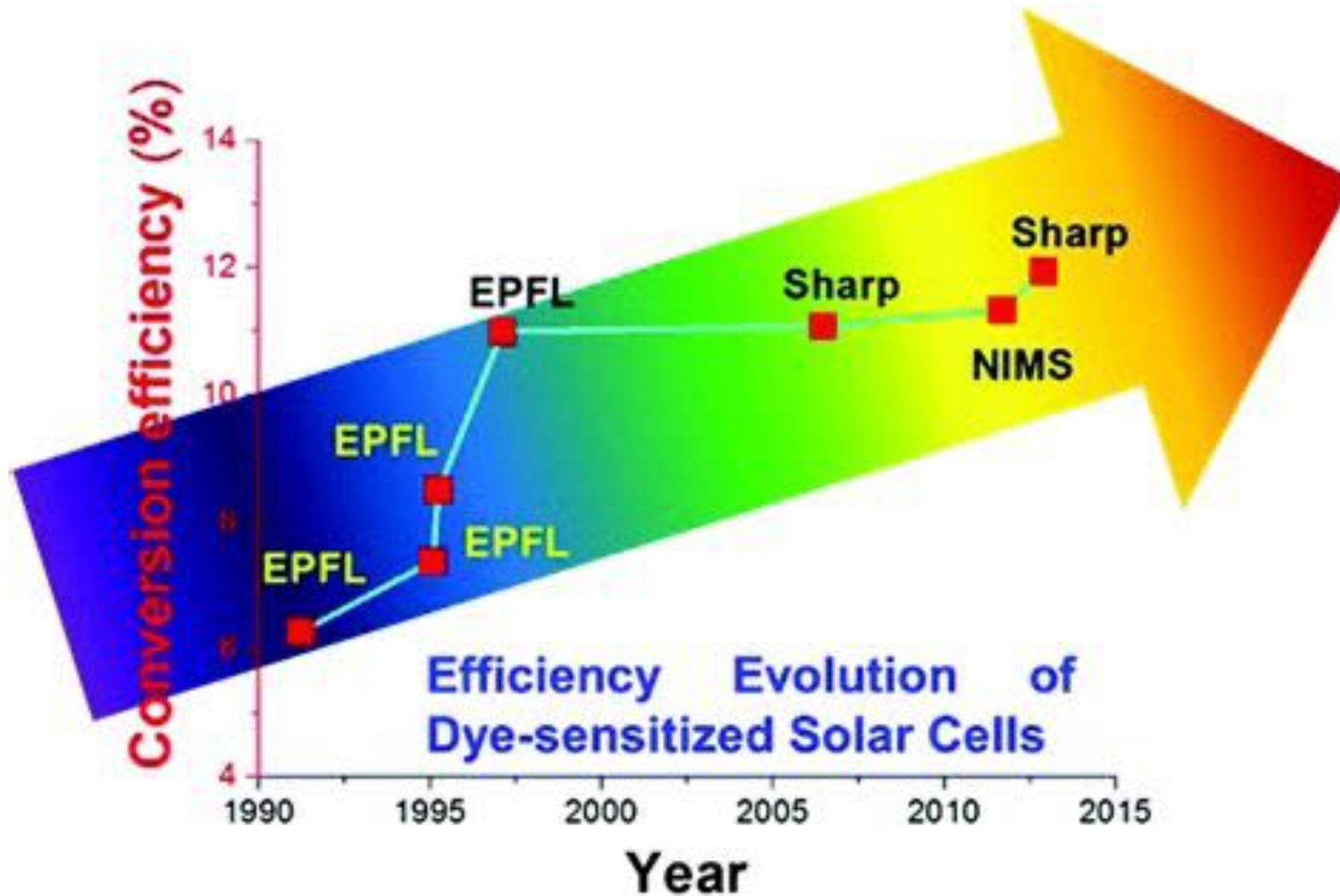
- Dye sensitized solar cell help in broader wavelength light absorption in visible region
- Need of suitable redox couple
- Can enhance the charge separation and transfer to the electrode/electrolyte interface
- Can protect the underlying inorganic photoelectrode
- But the charge transport in the dye is limited to short range especially with molecular materials
- Low cost liquid junction solar cell compared to Photovoltaic
- Efficiency improvement are done

DSSC – Photoinduced redox reactions

Photo induced redox reactions in DSSC

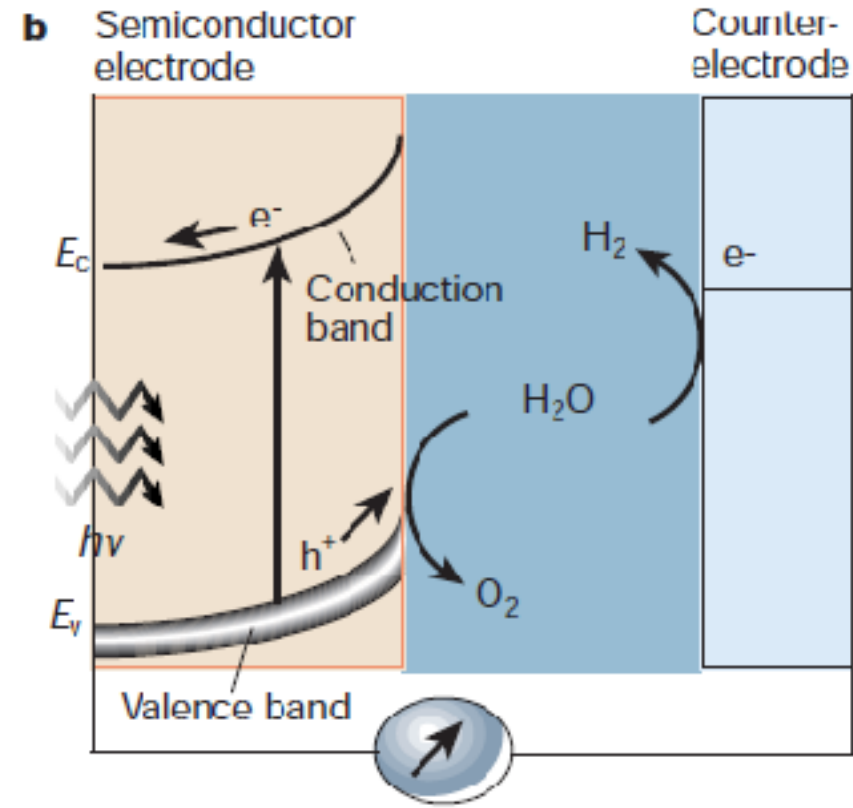


Dye sensitized solar cells



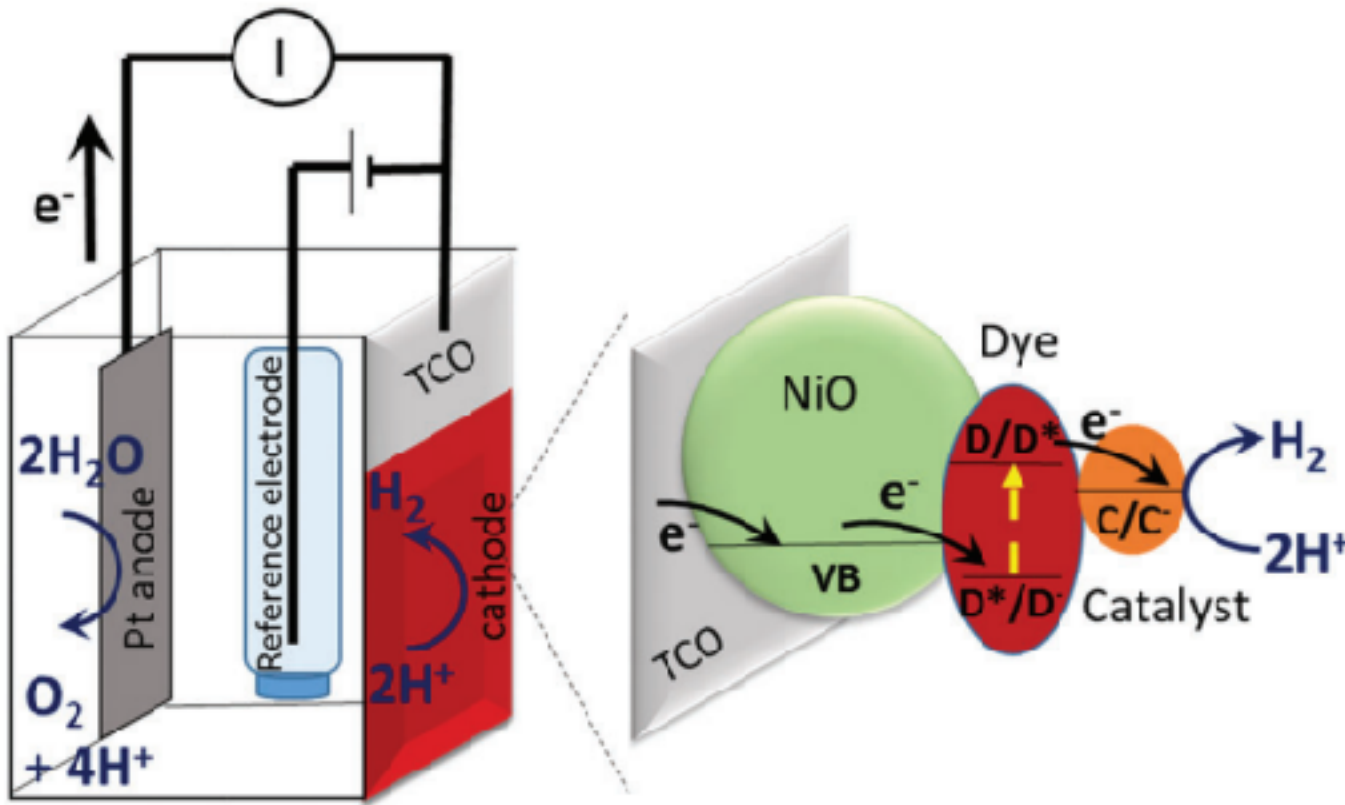
Photoelectrodes - photoelectrosynthesis

- n-type photoelectrodes for photooxidation (water oxidation)
- P-type photoelectrodes for reduction reactions (Hydrogen evolution, CO_2 reduction, nitrogen reduction or nitrogen fixation)
- Photoelectrosynthesis of solar fuel with smaller number of hydrocarbons (ethane, methane, methanol, acetic acid)



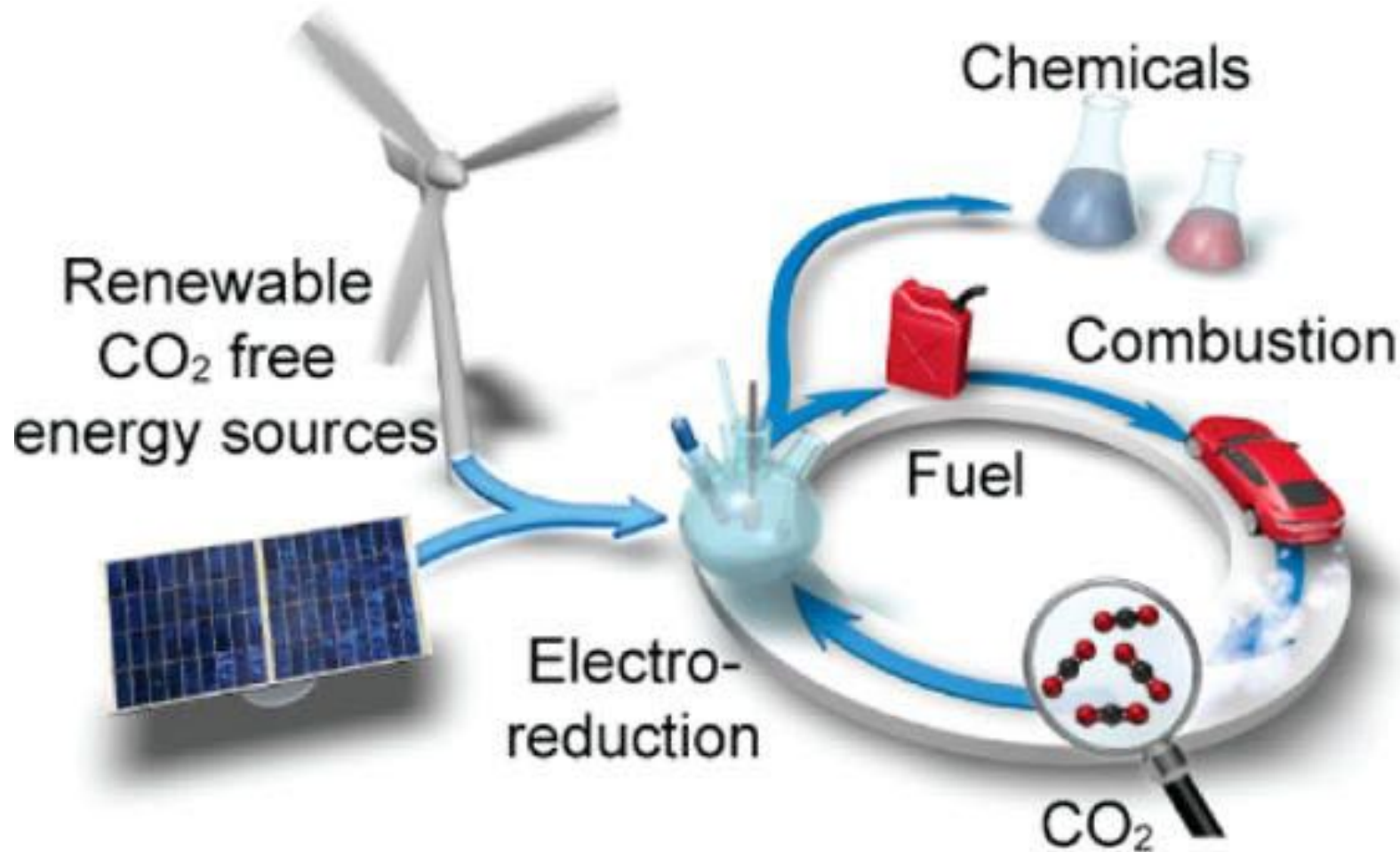
b. Photoelectrochemical
solar to fuel cell

Photoelectrodes in photoelectrosynthesis



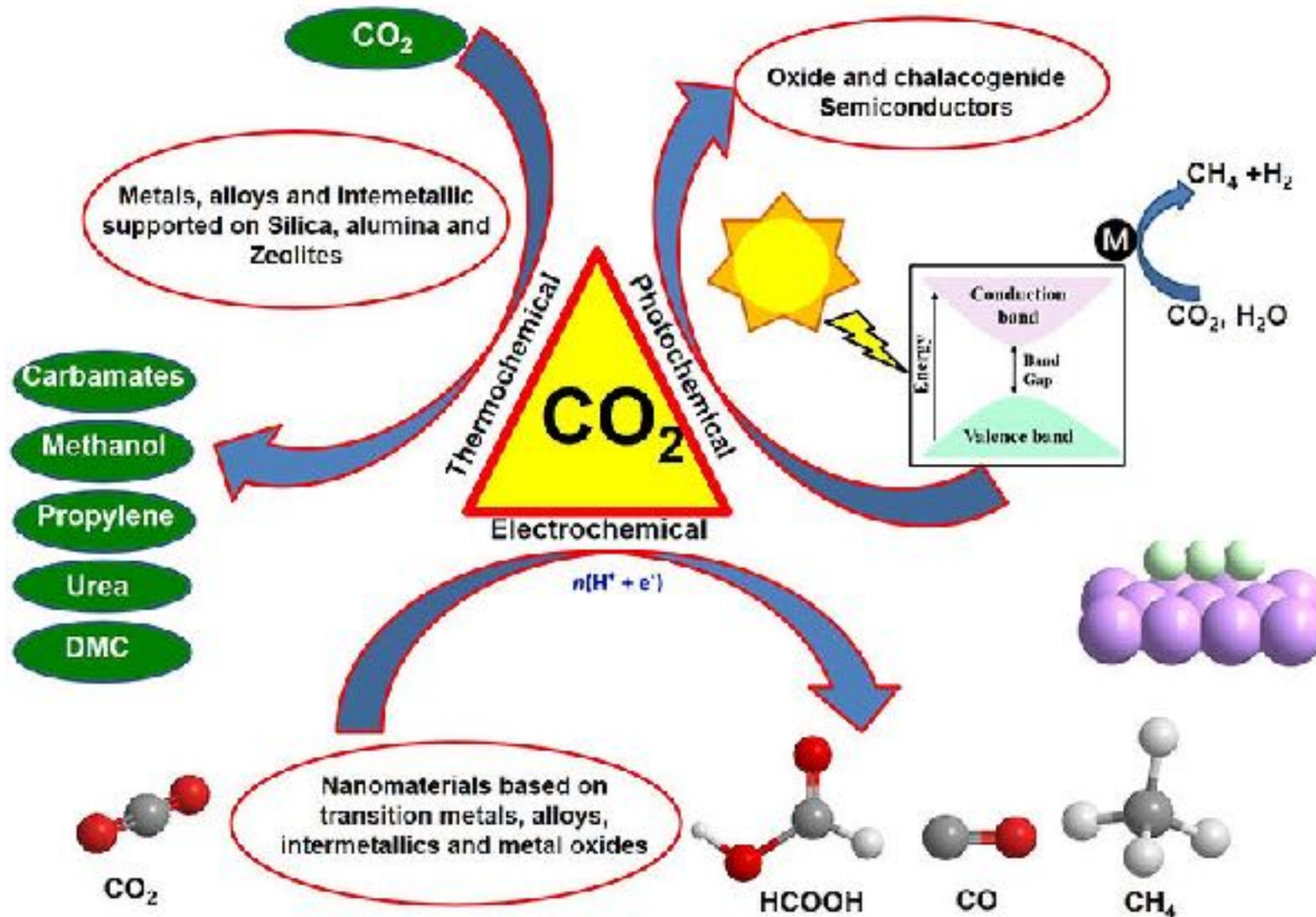
- Dye for sensitization and broad spectrum light absorption
- Works on the principle of redox shuttling to generate Reversible solar cell
- Can enhance the charge separation and injection
- Protect the underlying inorganic semiconductor photoelectrodes
- Solar fuel generation

Carbon dioxide reduction -Electrosynthesis



- Need of clean fuel technology
- Carbon dioxide capture and recycling to chemicals using electrochemical methods
- Reduce the fossil fuel consumption
- Use the PV-electrosynthesis cell

Carbon dioxide reduction -photoelectrosynthesis



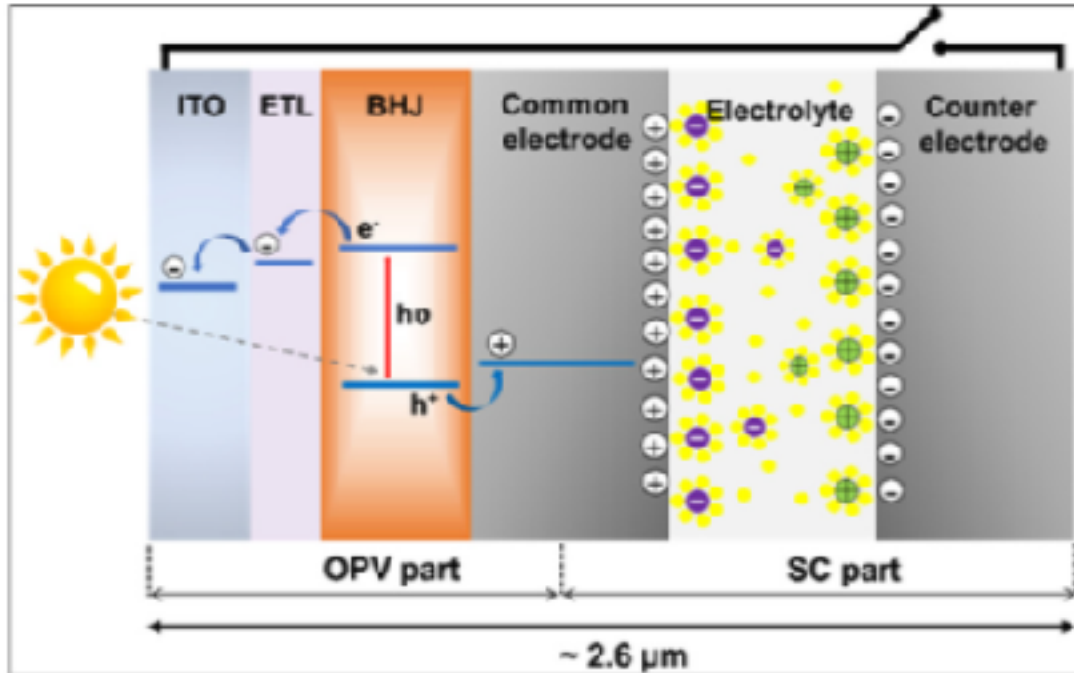
Photoelectrochemical carbon dioxide reduction using semiconductors

Conduction band in photocathode favour reduction of CO₂ to useful small chemicals

Helps to alleviate the global warming problem – CO₂

Efficiency and selectivity should be improved

Solar batteries



- Direct conversion of solar energy in battery charging
- Back side with transparent cover allows light to pass through
- One electrode can be light absorbing
- This will charge the battery by favouring the redox reaction at anode and cathode
- Need of photochargeable materials
- Thin film photoelectrode – battery material
- Efficiency must be improved
- Selective anode or cathode reaction should be favoured by photochargeable battery material
- This will be future for direct solar energy conversion to charge storage devices