

# Z-Scheme Dye Cells for Solar Fuels

## Buried Junctions vs Chromophore-Catalyst Assemblies

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### ABSTRACT

In general, the redox reactions that yield fuels require greater photopotentials than can be created by absorption of a single photon. As a result, cell architectures for solar fuels are under study that utilize a two-photon configuration (Z-scheme), in which one pair of photogenerated charge carriers recombine to up-convert their energy into additional photopotential (Fig. 1). In one scheme based on molecular chromophores and molecular catalysts combined in a dyad structure (Fig.1(b)), the photopotential for photoelectrosynthesis to fuel is determined by the difference between the oxidative and reductive potentials of molecular catalysts rather than the difference between the Fermi levels within the semiconductors. In a second alternative configuration the photopotential needed for photoelectrosynthesis is generated in a buried-junction Z-scheme configuration, as depicted in Fig.1(a). In this cell, the photon-absorbing and voltage-generating region is encapsulated within TCO layers and isolated from the solution redox chemistry. This architecture has the advantage of avoiding photo-corrosion and separating the product evolution onto the two planar outer surfaces while using molecular catalysts to perform the redox processes.

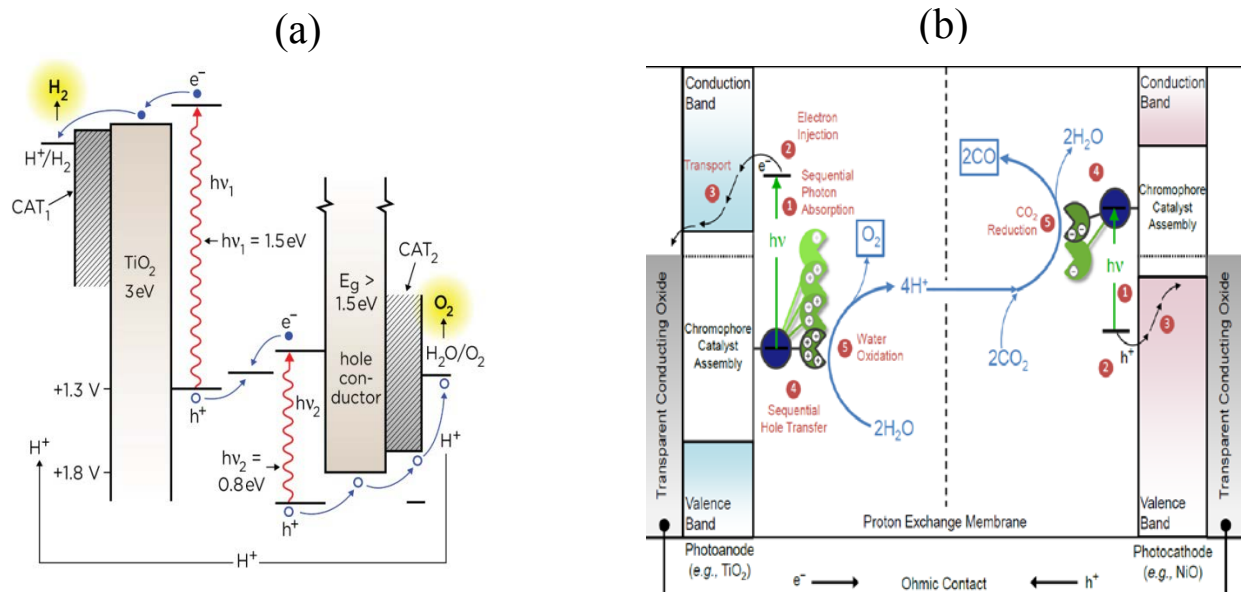


Figure 1. Dye sensitized Z-scheme solar cells for  $\text{H}_2\text{O}$  splitting. (a) Buried junction architecture. (b) Unburied junction chromophore-catalyst assembly (University of North Carolina EFRC).

The differences and advantages/disadvantages of the two types of Z-schemes are summarized below in Table 1.

TABLE 1

Unburied vs Buried Junctions for Solar Fuels

Unburied PEC Junctions

Redox potentials of chromophores have to align appropriately a priori with energetic req'mts (redox couples) of both redox reactions as well as with the NC n- and p-type charge conducting supports.

Excited states of Chromophores are in contact with reactant solution and photocorrosion could be an issue.

Gaseous products produced (H<sub>2</sub> or O<sub>2</sub> or C-H-O fuel) is released on nanoparticle surfaces in charge-conducting NC film support, which could lead to mechanical disruption of the film or diffusion issues out of the film.

Diffusion limitations are greatly reduced since the protons generated at the anode and needed at the cathode are produced at coplanar electrodes facing each other.

Buried PEC Junctions

Redox potentials of chromophores only have to align appropriately with band positions of NC supports. They move automatically to the proper positions wrt the redox couples of the electrode reaction if the photovoltage is sufficient to drive the electrochemical reactions.

Excited states of chromophores are not in direct contact with the reactant solution, mitigating photocorrosion of chromophores.

Gaseous products are released on the outer planar dark electrode surfaces of the cell and cannot disrupt the NC film.

Alleviation of diffusion problems requires a third electrode (dark cathode) that faces the anode, or a perforated or porous photoanode that allows easy proton transport (described in literature).