Coupled semiconductor- where is the Fermi Levels or do they have different redox properties

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There has been anxiety to extend the light absorption to visible range, while employing mainly titanium dioxide based semiconductors. The motivation for this is to maximize the use of available solar radiation. Though various experimental strategies have been adopted to sensitize the semiconductor to visible range, the concept of "coupled semiconductors" has been receiving increasing attention these days. The principle of this concept is to couple another semiconductor which could absorb radiations in the visible range, but the energy levels, namely the top of valence band and the bottom of the conduction band are energetically at positions for easy transfer of both the electron and hole (exciton) or at least one of them namely the electron in a downhill fashion. The relative energetic positions of the coupled semiconductors are shown in Fig.1.

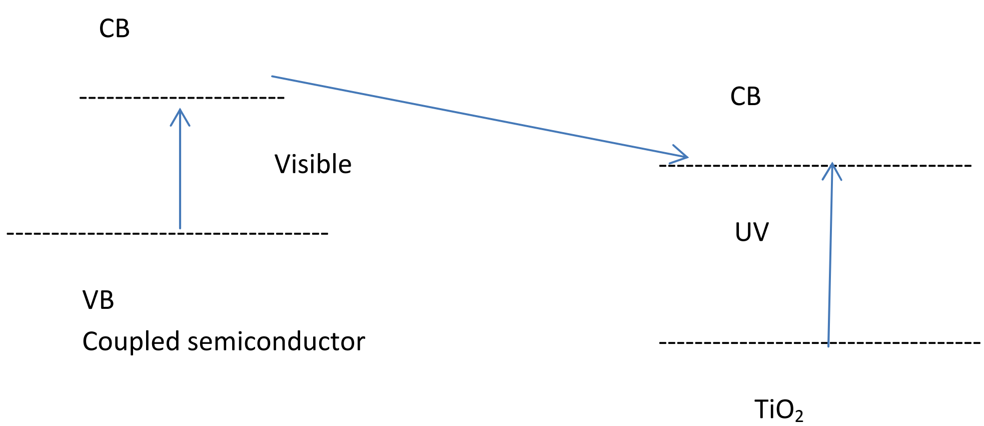


Fig.1. The relative energy positions of VB and CB for both the semiconductors

The excited electron in the conduction band of the semiconductor is energetically at less negative value and hence takes more stable allowable energy state in $TiO_2$ conduction band thus promoting the reduction reaction especially in hydrogen evolution reaction in water splitting.

This argument holds good only when the energetics of allowed states in semiconductors remain in tact when they are brought together. However, it is generally believed that when two conducting systems are brought together, the Fermi levels will be at the equal position. This postulate holds good for semiconductor/electrolyte interface or for two metallic systems. This may be true for systems where two semiconductors for a single solid solution. This is clear from the optical spectrum of these materials which normally show a single value for the absorption indicating a single valued band gap.

Based on this observation, one may presume that in the so called coupled semiconductors as well depending on the extent and strength of contact, there can be some kind of mixed phase at the interface and at least at this region the so called optical band gap can assume a unique and fixed value d in between the values of the two semiconductors involved. Under these circumstances, it is possible to promote the reduction reactions by the excited electrons and the hole can still promote the oxidation with different redox levels. The points that arise out of this argument are:

(i) How far it is true that the optical band gaps of the two coupled semiconductors remain intact as they were when the semiconductors are not coupled?

(ii) Do the Fermi levels in the two semiconductors remain as it was in the individual semiconductors?

(iii) The enhanced photo-catalytic activity normally observed with coupled semiconductors should be comparable to that observed on low band gap semiconductor.

It is possible that the arguments given in this short write up could be totally wrong and one should still consider as is done in most of the literature on this topic of coupled semiconductor operating in unison but still retain their individual character.