CHAPTER 6
SOME FUNDAMENTAL ASPECTS OF PHOTOCATALYSIS

Semiconductors with high ionicity are stable against corrosion and passivation. However, they require the ultra violet region of the electromagnetic spectrum. As stated earlier, threshold behaviour is important in photo-electrochemistry to maximize the use of solar spectrum. In this sense, for water decomposition materials with band gap between 1.3 to 1.8 are the optimum type of semiconductors for maximizing the efficiency of the water decomposition reaction. This means one wishes to make use of the visible range of the solar spectrum.

Light absorption by a semiconducting solid is governed by Beer's law

$$A = \ln (I/I_o) = \alpha l \qquad \text{or } T = (I/I_0) = \exp (-\alpha l)$$

Where I and I_0 – transmitted and incident light intensity and α is called the absorption coefficient. Semiconductors can be classified as direct or indirect band semiconductors. Direct band gap semiconductors have large absorption coefficient (10^4 -10^5 cm^{-1}).

The absorption coefficient for these materials are given by the equation,

$$\alpha = [A(h\nu – E_g)^m] /h\nu$$

In this equation m is a constant which depends on the optical transition, m=2 for an indirect band gap semi-conductor and ½ for a direct band gap semi-conductor.

Intrinsic carrier concentration in semiconductors is normally low and the equation concerning this parameter is given by

$$N_j p_i \; \alpha \; \exp(-E_g/kT)$$

Doping generally increases the conductivity of the semiconductor and able to control other electronic properties. Doping with other valent ions or even the crystal defects can also behave as dopants. Therefor conductivity can be controlled by doping and is given by the expression

$$\sigma = qn\mu_n + qp\mu_p$$

Where μ_n and μ_p are the charge carrier mobilities

The processes that take place on a semiconductor powdered material can be visualized as follows:
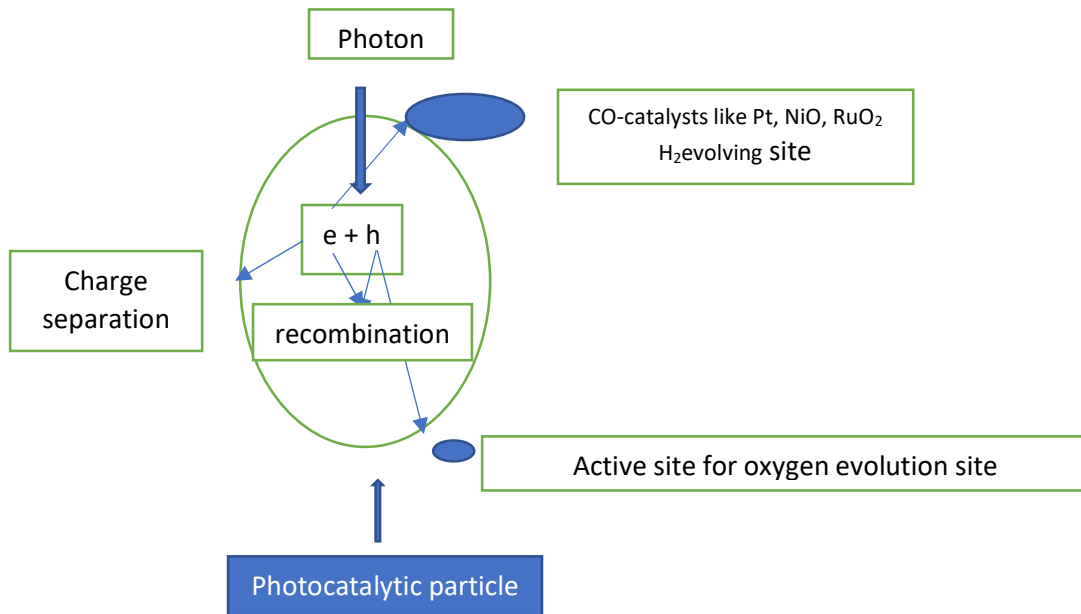
At this stage, we need to understand the structure of electrode-electrolyte interface and the possibility of charge transfer when the electrode happens to be a semiconductor. The charge transfer depends on the relative energy positions of the donor and that of the acceptor. Flat band potential is defined no band as Flat bending situation and for highly doped semiconductors, this equals the bottom of the conduction band. This is defined by the following equation:

V_{fb} = $E_0 - \chi$ + (1/2) E_g where χ is the value of electronegativity in Mulliken's scale.

Typical model calculation is shown below. Let us consider for model calculation the semiconductor TiO_2. The band gap of this semiconductor was taken as 3.2 eV. The values of electron affinity and ionization energy of Titanium and oxygen are respectively, 0.08 and 1.46 eV and 6.81 and 13.6 eV. The elements electronegativity is given by arithmetic mean values and are respectively 3.44 and 7.53 respectively. The semiconductor electronegativity is given by geometric mean and there are three elements in the semiconductor chosen is given as $[3.44 \times (7.53)^2]^{1/3}$ = 5.79. The value of the conduction band minimum is given by $\chi - E^e - 0.5 \times E^g$ = 5.79-4.5-(0.5X3.2) = -0.31 eV. The valence band position can be -0.31+3.2 = 2.89.

The charge transfer abilities of a semiconductor electrode depend on whether there is an accumulation or depletion layer. If there is an accumulation layer then it

behaves as metallic electrode, since excess of majority charge carriers available for charge transfer.

If there is a depletion layer then there are few charge carriers available and the electron transfer reaction occurs slowly. However, if the electrode is exposed to radiation of sufficient energy, electron hole pairs are produced. If the processes occur within the interior of semiconductor, the heat and recombination take place. If it occurs in the space charge region, the electric field in this region will cause the separation of the charge.

1, Sufficiently high (visible) light absorption

2. High stability in dark and under illumination (no photo corrosion)

3. Suitable band edge positions to enable the reduction/oxidation of water by the photo generated holes /electrons

4. Efficient charge transport in the semiconductor

5. Low over potentials for the reduction/oxidation reaction (high catalytic activity).

Stability against photo corrosion

Most important property which limits the usefulness of many photo-active materials. Many non-oxide semiconductors (Si, Ga As, GaP, and so on) either dissolve or form a thin oxide film which prevents the electron transfer across the interface.

Most of the M-O photo anodes are thermodynamically unstable. Eg: TiO_2 and SnO_2 show excellent stability over a wide range of pH and applied potential. ZnO always decomposes, Fe_2O_3 shows an intermediate case (pH and oxygen stoichiometry)

Requirement of band positions:

Conduction and valence band edges should straddle the reduction and oxidation potential of water. Specifically E_{CB} should be above or less in numerical value E_{red} and E_{VB} should be below or more numerical value of E_{ox}.

The exciton life time is an important criterion that is the hole transfer across the n type semi- conductor-electrolyte interface. It should be fast enough to compete with photo-corrosion and to avoid accumulation. Loading of metals like Cu, Ag, Au, Ni, Pd, Rh and Pt over a variety of metal oxide semiconductors results efficient charge

separation. Pt is well known as an excellent co catalyst for hydrogen evolution. The addition of carbonated salts or other electron mediators enhance the hydrogen production by preventing backward reaction.

Mixed metals oxide semiconductors NiO over $SrTiO_3$ – $NiO(H_2)$, $SrTiO_3$ (O_2) RuO_2 over TiO_2 -30 times bigger activity than TiO_2 alone. But if the concentration of RuO_2 exceeds a limit- acts as electron hole recombination centers, In the presence of co-catalysts such as NiO –highly active niobates, titanates and tantalates are reported ($NiO/NaTaO_3$).

Visible light activity

There are methods by which photocatalysts can be fabricated, by which they respond in the visible light. Valence band formation using elements other than oxygen. Some other oxygen containing multicomponent systems are also useful typical examples are $BiVO_4$, $AgNbO_3$, Ag_3VO_4, $Ca_2 Bi_2 O_4$.

Ion doping

Cation doping - transition metals (V, Cr, Fe, Mo, Ru, Os, Re, Rh, V, etc.) -rare earth metals and these doped ions create new (impurity) energy levels. Metal ion dopants act as electron or hole traps

Doping of anions such as N, F, C, Si in metal oxides or mixed metal oxides can shift in photo response into the visible region. These systems show little tendency to form recombination centers. Another remarkable thing is construction of Z-scheme systems. Dual semiconductor systems, and Dye-sensitization are other methods to shift the photon absorption wavelength.   Dye molecules absorb light with the transfer of an electron from the ground state to excited state. The excited electron may then transfer to the conduction band of an appropriate metal oxide participate in the reduction reaction.

References:

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