Chapter 3

GENERAL PRINCIPLES OF PHOTOCATALYSIS

The scope of photocatalysis is increasing day by day. However, the field of decontamination of pollutants (including some drug and dye molecules) has received considerable attention. This aspect will be dealt with in detailed manner in a separate chapter. The activation and conversion of stable molecules like water. Carbon dioxide and dinitrogen still attract the attention of scientific community. In Figure 1, the various processes promoted by photocatalysis by semiconductors are shown.

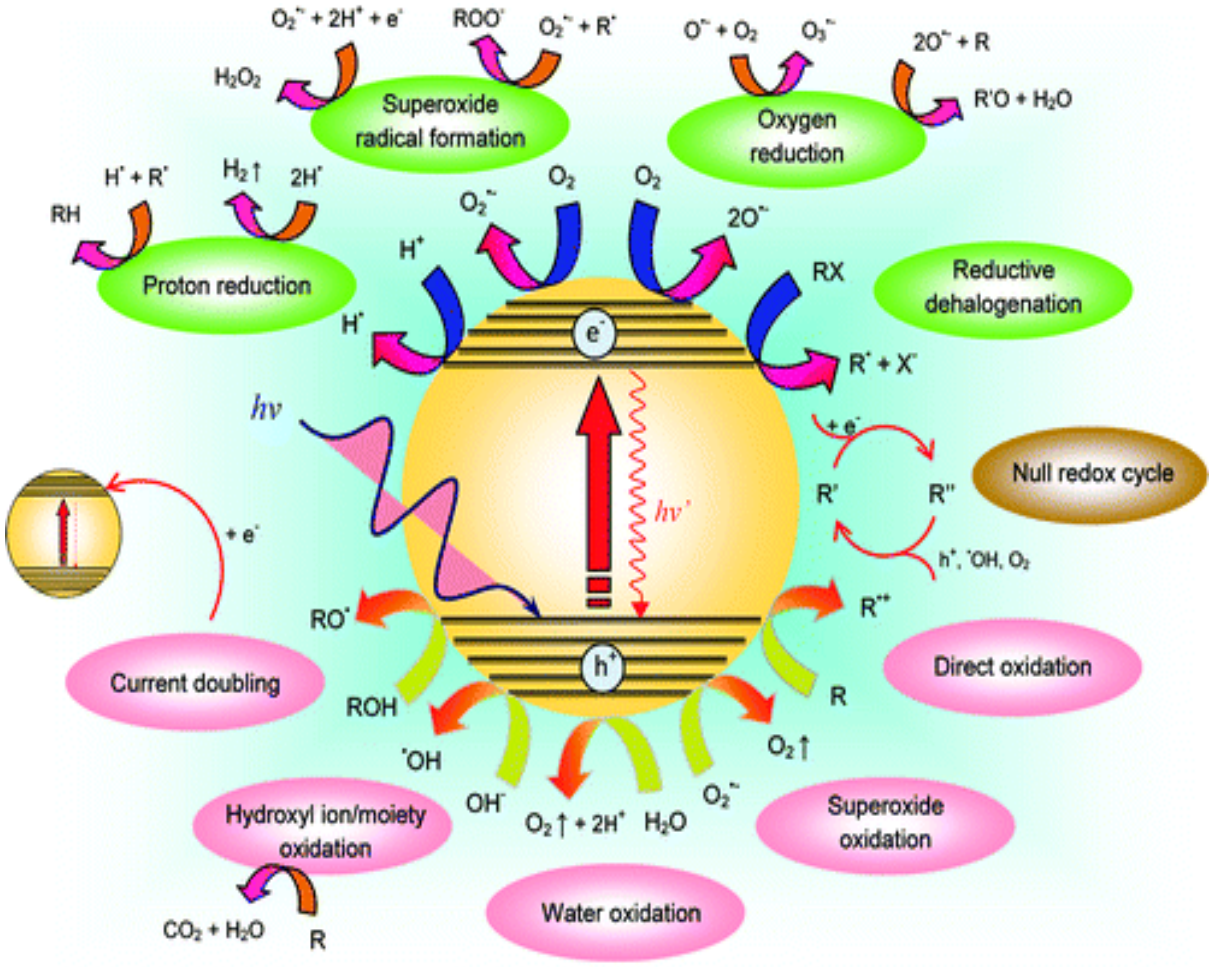

Fig. 1 Various light induced reactions involved in semiconductor photocatalysis [Reproduced from reference Tech et al., J. Phys. Chem. Lett., 3, 629-639 (2012)].

It is seen a variety of oxidation and reduction reactions can be carried out as a result of photo-catalysis. In addition, a host of organic reactions and radical induced inorganic transformations can be promoted in this field. The basic

principles involved in this type of photocatalytic reactions are shown in Figure 2 using TiO_2 as a typical photocatalyst. The photon absorption gives rise to an energic electron in the conduction band which can be utilized for the reduction (acceptor) reaction and the hole formed in the valence band can be utilized in the oxidation (donor) reaction.

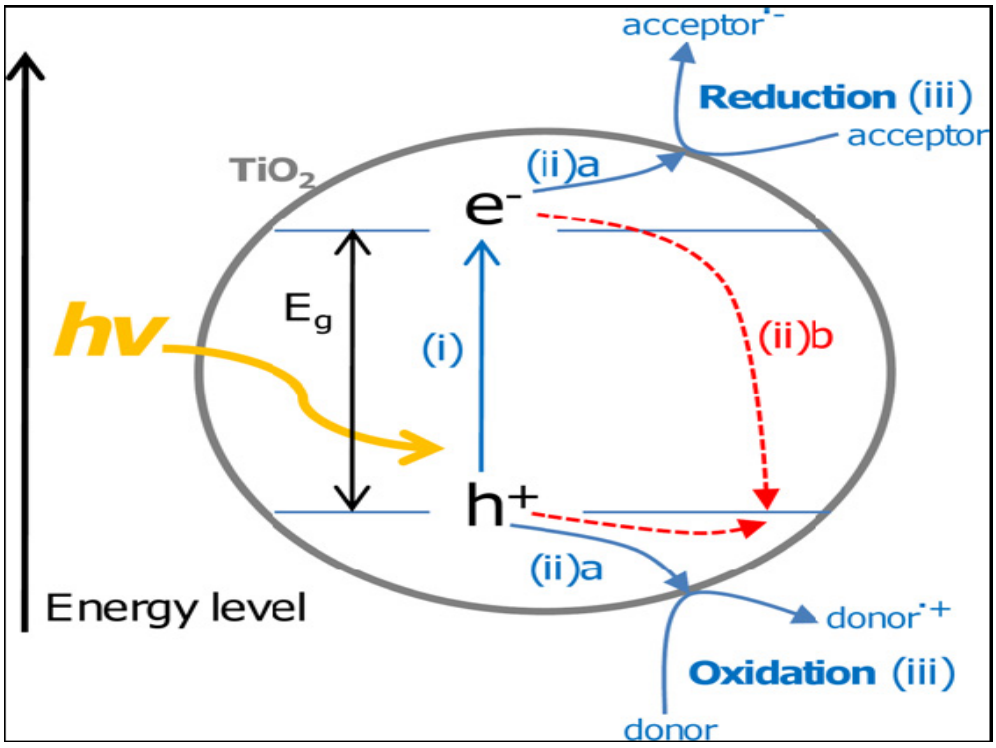

Fig. 2. Various processes involved in semiconductor photocatalysis. (i) Photon absorption and electron–hole pair generation. (ii) Charge separation and migration; (iia) to surface reaction sites or (iib) to recombination sites. (iii) Surface chemical reaction at active sites.[Leary et al carbon, 49. 741-772 (2011)].

Various Methods for Improving the Efficiency of Photocatalyst

These attempts are mainly concerned with facilitating the charge transfer efficiency/. This can be achieved in many ways. Among them, is to alter the energy position of Fermi level of the semiconductor. In addition. it is possible to introduce the electron transfer agents or hole trapping species. For electron transfer process, one has to use agents which have high electron affinity and these are mostly noble metals. Like Au, Pt and so on. This situation is pictorially shown in Figure 3.

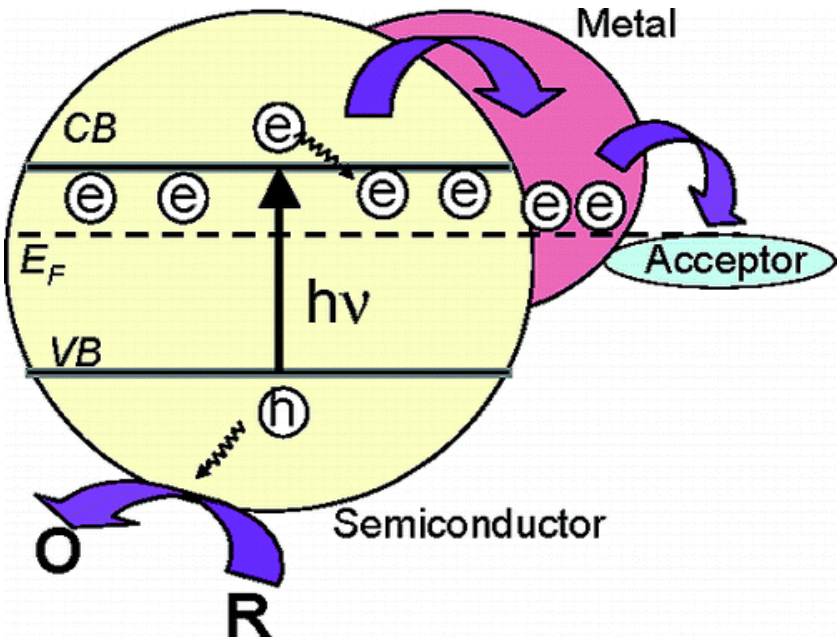

Fig. 3 Metal deposited semiconductor to facilitate electron transfer to the acceptor species. Refer to Subramanian et al., J. Am. Chem. Soc. 2004, 126, 4943-4950.

2. **Coupling of two Semiconductors**:

Another way to achieve efficient electron traanfer and decrease recombination of charge carriers is coupling two semiconductors. This can also be useful to use longer wavelenth radiaation that is shifting the photon source from UV to visible range. This has to satisfy that interfacial electron transfer between two semiconductors with different conduction band edges will facilitate and also minimize electron-hole recombination. The possibility is illustrated in Figure 4.

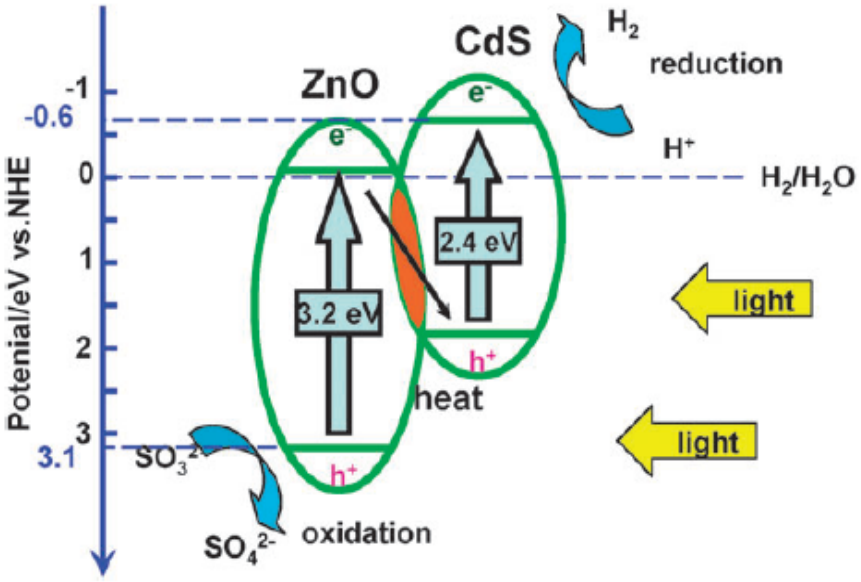

Fig. 4. Coupling of two semiconducotrs. Note the relative positions of the conduction band minima of the two semiconductors. See for example Wang et al. *Chem. Commun.*, **2009**, 3452–3454.

3.**Sensitization**

Usually this is done by employing substances (Dyes or other photoactive materials) which will absorb radiation. The separation and transfer of the charges like in splitting of pure water was achieved with dye-coated photocatalyst which is attributed to good electronic contact between dye and photocatalyst. This is pictorially shown in Figure 5.

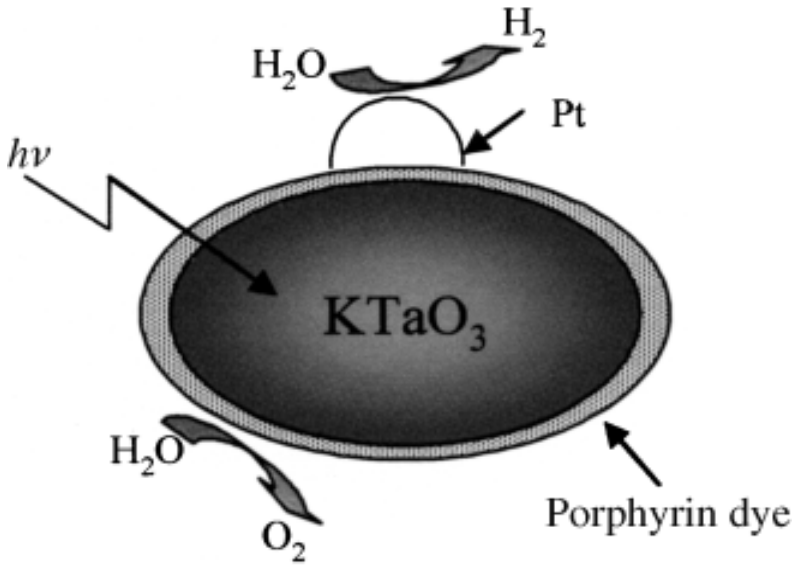

Fig.5 Dye coated semiconductor and the dye absorbs radiation or facilitate the charge transfer See for example Hagiwara et al. *Angew. Chem. Int. Ed*., 2006, 45, 1420–1422.

4. Doping with metal ions (Fe^{3+}, V^{5+} etc.) and non-metals (N, C, S etc.)

The doping process helps to introduce additional states in the semiconductor eg.TiO_2 thereby reducing the band gap and improving the visible light absorbing properties. The main drawbacks of these systems are (1) The new energy states introduced into the composite material can also act as recombination centers for excitonic species especially when dopant concentration is high and (2) the thermal stability of the material will be affected.

There are other possibilities of activating and facilitating charge transfer process which will be taken up subsequently.