

CHAPTER III

SEMICONDUCTOR PHOTOCATALYSIS

The semiconductor photocatalysis has been found to be active in the treatment of wastewater for the destruction of several, also toxic and bioresistant, organic pollution.^{1,2,3,4,5,6}

Semiconductors (e.g., TiO_2 , ZnO , Fe_2O_3 , CdS , and ZnS) can act as sensitizer for light-reduced redox process due to their electronic structure, which is characterized by a filled valence band and an empty conduction band . When a photon with an energy of $h\nu$ matches or exceeds the bandgap energy, E_g , of the semiconductor, an electron is promoted from the valence band, VB, into the conduction band, CB, leaving a hole, H_{vb}^+ , behind (see Figure 3.1). Excited state conduction band electrons and valence-band holes can recombine and

¹ Vinodgopal, K., and Kamat, P.V., "Enhanced rates of photocatalytic degradation of an azo dye using $\text{SnO}_2/\text{TiO}_2$ coupled semiconductor thin films", *Environ. Sci. Technol.* 29 (1995) : 841 - 845.

² Tanaka, K., Hisanaga, T., and Harada, K., "Photocatalytic degradation of organohalide compounds in semiconductor suspension with add hydrogen peroxide", *New J. Chem.* 13 (1989) : 5 - 7.

³ Tanaka, K., and Abe, K., "Degradation of phenol, asulam and lignin in aqueous solution by ozonation", *Toxicological and Environmental Chemistry* 54 (1996): 187 - 193.

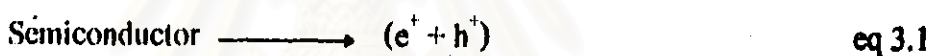
⁴ Herrmann, J.M., Guillard, C., and Pichat, P., "Heterogeneous photocatalysis: an emerging technology for water treatment", *Catalysis Today* 17 (1993) : 7 - 10.

⁵ Bard, A.J., "Photoelectrochemistry and heterogeneous photocatalysis at semiconductors", *Journal of Photochemistry* 10 (1979): 59 - 75.

⁶ Sangchakr, B., Hisanaga, T., and Tanaka, K., "Photocatalytic degradation of sulfonated aromatics in aqueous TiO_2 suspension", *Journal of Photochemistry and Photobiology. A: Chemistry* (1994) (Draft).

dissipate the input energy as heat, get trapped in metastable surface states.^{7, 8, 9, 10}

Unlike metal, semiconductor lack a continuum of interband states to assist the recombination of the electron hole pair. This assures an electron-hole pair lifetime sufficiently long to allow these species to participate in interfacial electron transfer. Thus, the act of photoexcitation usually generates an electron-hole pair poised respectively at the conduction band and valence band. The component of this activated pair, when transferred across the interface, are capable, respectively of reducing and oxidizing a surface-adsorbed substrate, forming on a common surface a single oxidized electron donor (D) and singly reduce electron acceptor (A) (eq.3.2 and 3.3).¹¹



⁷ Davi, E., Palmisano, L., and Sclafani, A., "Photocatalytic degradation of phenol by TiO₂ aqueous dispersions: rutile and anatase activity", *New J. Chem.* 14 (1990) : 265 - 268.

⁸ Bard, A.J. "Photoelectrochemistry and heterogeneous photocatalysis at semiconductors", *Journal of Photochemistry* 10 (1979): 59 - 75.

⁹ Hoffmann, M.R., Martin, S.T., Choi, W., and Bahnemann, D.W., "Environmental applications of semiconductor photocatalysis", *Chem. Rev.* 95 (1995) : 69 - 96.

¹⁰ Fox, M.A., and Dulay, M.T., "Heterogeneous photocatalysis", *Chem. Rev.* 93 (1993) : 341 - 357.

¹¹ Ibid.

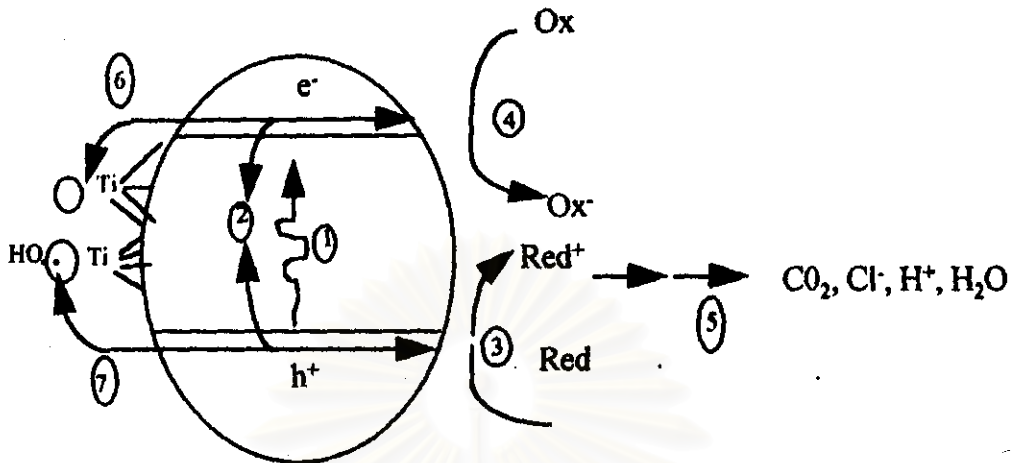


Figure 3.1 Primary steps in the photoelectrochemical mechanism: 1) formation of charge carriers by a photon; 2) charge carrier recombination to liberate heat; 3) initiation of an oxidative pathway by a valence-band hole; 4) initiation of a reductive pathway by a conduction-band electron; 5) further thermal (e.g., hydrolysis or reaction with active oxygen species) and photocatalytic reaction to yield mineralization products; 6) trapping of a conduction-band electron in a dangling surficial bond to yield $Ti(III)$; 7) trapping of a valence-band hole at a surficial titanol group.

These radical ions (D^{\bullet} , A^{\bullet}) can participate in several pathways:

- 1) They may react chemically with themselves or other adsorbates.
- 2) They may recombine by back electron transfer to from the excited state of one of the reactants or to waste the excitation energy by a nonradiative pathway.
- 3) They may diffuse from the semiconductor surface and participate in chemical reaction in the bulk solution.

However the rate of redox processed depends on the several factor, among which the most important are

- a) intensity of radiation absorbed by the semiconductor,
- b) hole-electron pair formation and recombination rate,
- c) charge transfer rate,
- d) reagents and products adsorption and desorption rate,
- e) pH, and f) preparation method of the semiconductor.¹²

or when immobilized in a fluidized bed reactor retain much of their native activity after repeated catalytic cycles.

Semiconductor photocatalysis can be more appealing than the more conventional chemical oxidation methods because semiconductors are inexpensive, nontoxic, and capable of extended use without substantial loss of photocatalytic activity. Furthermore, semiconductor particles recovered by filtration or centrifugation or when immobilized in a fluidized bed reactor retain much of their native activity after repeated catalytic cycles.

The TiO_2 photocatalytic reaction is now generating commercial interest because of its low cost, simplicity, robustness, and ability to achieve extremely low residual organic contaminant levels.¹³ TiO_2 is produced in two

¹² Davi, E., Palmisano, L., and Sclafani, A., "Photocatalytic degradation of phenol by TiO_2 aqueous dispersions: rutile and anatase activity", *New J. Chem.* 14 (1990) : 265 - 268.

¹³ Dong, H.K., and Marc, A.A., "Photoelectrocatalytic degradation of formic acid using a porous TiO_2 thin-film electrode". *Environ. Sci. Technol.* 28 (1994) : 479 - 483.

crystal forms, rutile and anatase.¹⁴ Rutile form has shown, on the contrary, inability or negligible activity for the photodegradation of organic pollutants. Photoactivation of TiO_2 requires are radiation whose wave length must be lower than or, at least equal to 384 nm.¹⁵

Many photocatalytic reactions (at solid-liquid interface) follow the langmuir-Hinshelwood Kinetic model. This model assumes that:

- 1) At equilibrium, the number of surface adsorption sites is fixed;
- 2) Only one substrate may bind at each surface site;
- 3) The heat of adsorption by substrate is identical for each site and is independent of surface coverage;
- 4) There is no interaction between adjacent adsorbed molecules;
- 5) The rate of surface adsorption of the substrate is greater than the rate of any subsequent chemical reaction; and
- 6) no irreversible blocking of active sites by binding to product occurs .

¹⁴ Checker, S.K., *Technology of pigments dyestuff & dye-intermediates* (Delhi : SBP), p. 105.

¹⁵ Davi, E., Palmisano, L., and Sclafani, A., "Photocatalytic degradation of phenol by TiO_2 aqueous dispersions: rutile and anatase activity", *New J. Chem.* 14 (1990) : 265 - 268.

Langmuir-Hinshelwood equation is

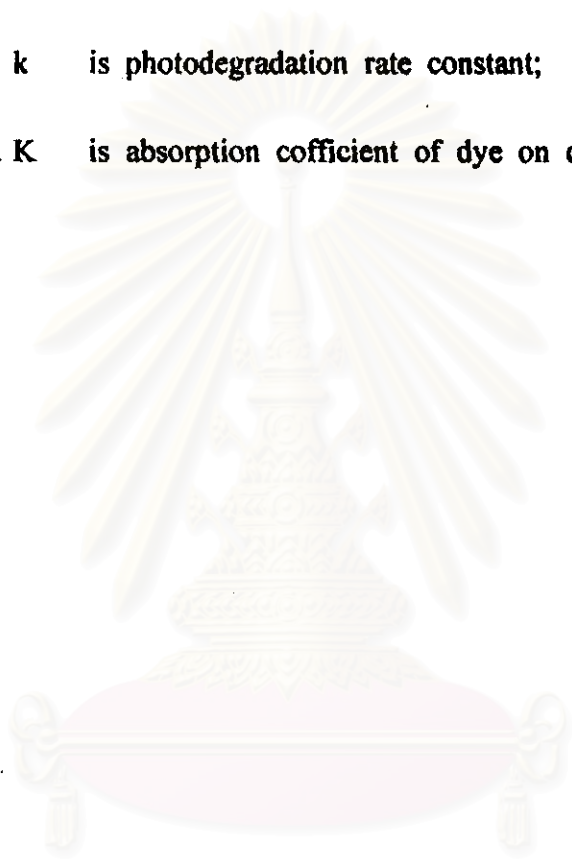
$$r_0 = kKC_0/(1 + KC_0) \quad \text{eq 3.4}$$

where r_0 is initial rate of photocatalytic degradation

C_0 is initial concentration of dye solution;

k is photodegradation rate constant;

and K is absorption coefficient of dye on catalyst.



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