Interfacial photocatalytic processes

Samina Ahmed
Institute of Glass and Ceramic Research and Testing (IGCRT), Bangladesh Council of Scientific and Industrial Research (BCSIR), Dhaka-1205, (BANGLADESH)
E-mail: shanta_samina@yahoo.com

ABSTRACT

This feature article highlights various aspects of interfacial photocatalytic processes including basic concepts, diverse applications toward a green and clean environment, photoelectrochemical approach and the developments made in this emerging field.
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KEYWORDS

Photocatalytic;
Photoelectrochemistry;
Interfacial;
Semiconductor;
Development.

PHOTOCATALYTIC TECHNOLOGY

Introduction

Semiconductor mediated photocatalytic technology for the destruction and decomposition of toxic and hazardous compounds has received considerable attention[1-6]. Over the past two decades, researchers throughout the world have particularly focused their attention on to this emerging photocatalytic technology. The reason behind getting such attention is its significant efficacy and easy-to-use operating procedure over the conventional biological and physico-chemical approaches, *e.g.* (i) adsorption, (ii) membrane filtration, (iii) coagulation, (iv) reverse osmosis, (v) air stripping etc. Nevertheless they do not destruct the pollutants but simply transfer the pollutant to another phase which again creates disposal problem. On the other hand chemical treatments, *e.g.* (i) chlorination, (ii) ozonation have the disadvantages of using strong oxidants such as chlorine and ozone which are hazardous in nature. However, photocatalytic technology as an advanced oxidation process (AOP) which promotes the degradation of pollutants through producing hydroxyl radicals as strong oxidizing agent and offers the following advantages:

i) The process is fairly simple since the natural UV component of the sunlight can trigger the photocatalytic process or it can be controlled just by switching on and off of the UV lamp;

ii) Usually non hazardous semiconductors (*e.g.* TiO_2, ZnO, Fe_2O_3) are used as the photocatalysts which decomposes the toxic substances to harmless products;

iii) There is no need to use expensive oxidants, since atmospheric oxygen itself plays the role of oxidant; and

iv) The mineralization product is harmless to the environment.

Although different types of semiconductor catalysts are available (*e.g.* TiO_2, ZnO, Fe_2O_3, CdS, ZnS, etc.), but to facilitate the successful photomineralisation of organic pollutants, an ideal photocatalyst must have the following features:

i. Highly photocatalytically active and photostable.

ii. Biologically and chemically inert.

iii. Insoluble in aqueous solution.

iv. High turnover number (*i.e.* number of product molecules per number of active sites and capable of entering into a large number of cycles).

v. Not harmful to the environment.

vi. Cheap and available; and

vii. Able to mineralize completely a wide range of hazardous and toxic compounds.

Considering the properties of the semiconductors, TiO_2 and ZnO appeared as the most promising photocatalysts due to their high photosensitivity, large band gap and non-toxic nature[5, 7-9]. Pure TiO_2 is cheap and widely available, thus it is commonly used in (a) white paint, (b) sunblocking material, (c) cosmetics, (d) vitamin tablets, and (e) scratch-resistant optical coatings. However, for the last two decades, this white pigment titania has been extensively used as the most effective photocatalyst to clean-up polluted water. TiO_2 has different crystalline forms. The most common forms are anatase and rutile[5,10,11]. The third crystalline form of TiO_2 is brookite, which is uncommon and unstable. The anatase and rutile forms are photoactive because of the presence of higher degree of surface hydroxylation. Generally, the TiO_2 – mediated photocatalysis process involves the oxidation of surface hydroxide groups, which actively participate in the photodegradation process. Thus, the higher degree of surface hydroxylation makes these two forms effective for a wide range of practical applications in various fields of environmental waste treatment. However a special form of TiO_2 (Degussa P25) is accepted and being used in many studies as the most effective research standard[10]. It is a typical non-porous composition of anatase : rutile, 70 : 30 with a BET (Brunauer-Emmett-Teller) surface area of 55 $m^2\ g^{-1}$ and a particle size of 30 nm in 0.1 mm diameter aggregates. It has a higher photocatalytic activity than any other readily available form of TiO_2. ZnO being an n-type semiconductor also exhibits many attractive features. It has a large number of active sites on the crystal surface which makes it a highly active photocatalyst. The wide band gap of ZnO (3.1 Ev) as compared to TiO_2 is capable to generate hydroxyl radicals effectively and ZnO absorbs more UV light. Hence, due to this high UV absorption efficiency more e^-/h^+ pair generates upon illumination which ultimately accelerates the photodegradation process.

The photocatalytic process is initiated due to the UV-excitation of semiconductor. Semiconductors are activated by absorbing ultra violet light, which causes transfer of electron from the valence band (VB) to the conduction band (CB). Hence photo-generated holes (h^+) and electrons (e^-) are formed simultaneously in the VB and CB respectively. The redox potential of the photogenerated valence band hole must be positive enough to produce adsorbed OH· radical, which is a strong oxidant (oxidation potential is 2.8 V relative to the standard hydrogen electrode). The hydroxyl radicals quickly attack the pollutant adsorbed onto the catalyst surface and in solution as well and can mineralize them into CO_2, H_2O etc. Indeed, hydroxyl radical is capable to break a wide range of pollutants into harmless products. On the other hand, the redox potential of the photogenerated conduction band electron must be negative enough to convert O_2 to superoxide anion which also takes part in degradation reaction. Figure 1 shows the mode of action of the photocatalyst towards the degradation process.
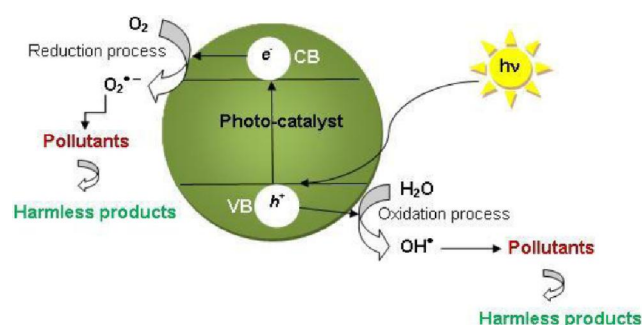

Figure 1 : Mode of action of the photocatalyst towards the degradation process

Diverse applications of photocatalyst

Photocatalytic technology is becoming more and more attractive to the researchers through out the world and consequently application of this technology has been diversified as shown in Figure 2. However, a number of TiO_2-based eco-friendly photocatalytic products have already been developed and commercialized[4] and TABLE 1. summarizes a list of TiO_2-based photocatalytic products[4].

Photocatalytic tiles have been developed[12] and an investigation was carried out to demonstrate the antibacterial effect. On conventional tiles, bacteria were found to survive upon exposure to light whereas on photocatalytic tiles there was no trace of bacteria after 1 hour illumination. The self-cleaning effect of TiO_2 coated tiles was

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also investigated[12]. On the regular tiles dirt adhered to the surface of the tiles while the photocatalytic tiles did not allow any dirt to stick to its surface. Cancer treatment is one of the most important issues which is associated with photocatalysis[3]. By using the strong oxidizing power of TiO$_2$ Fujishima *et. al.*[13] were able to kill the tumor cells. In another study Fujishima *et. al*[12] implanted cancer cells under the skin of mice to cause tumors to growth. When the tumors grew to about 0.5 cm, they injected the TiO$_2$ solution and then after 2/3 days they exposed the tumor and irradiated it. This treatment inhibited the growth of the tumor which was a promising result for the treatment of cancer using photocatalyst. This result encouraged them to develop a modified device with endoscope to allow the cancer to be exposed to
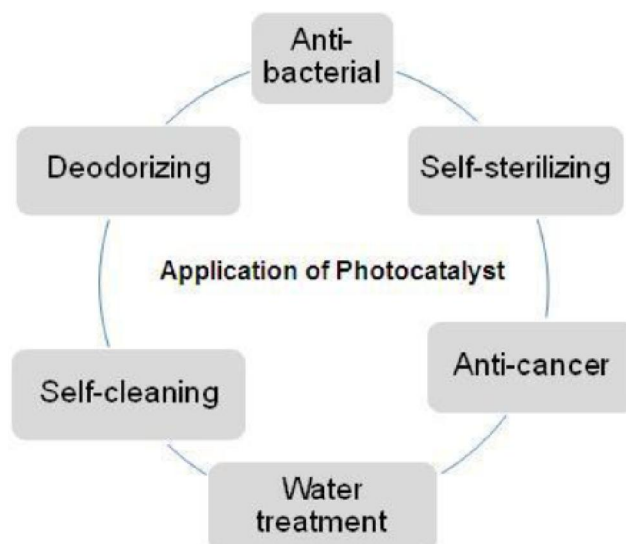

Figure 2 : Application of photocatalyst

TABLE 1 : A list of TiO$_2$-based photocatalytic products

Categories	Products	Properties
Exterior construction materials	Tiles, glass, tents, plastic films, aluminium panels	Self-cleaning
Interior furnishing materials	Tiles, wall paper, window blinds	Self-cleaning, antibacterial
Road construction materials	Soundproof walls, tunnel walls, lamp covers, traffic signs	Self-cleaning, air-cleaning
Purification facilities	Air cleaners, air conditioners, purification system for wastewater	Air-cleaning, water-cleaning, antibacterial
Household goods	Fibers, cloths, leathers, sprays	Self-cleaning, antibacterial

light while TiO$_2$ was being added to the tumor[3]. Using such device it should be possible to treat various parts of the human body containing cancer cells. TiO$_2$ coated photocatalytic antifogging glass is a successful development[12]. Usually, in case of normal glass when moist air becomes in contact with it, small droplets of water form on the surface of the glass and the glass becomes foggy. But on TiO$_2$ coated glass, the water forms a continuous flat sheet and causes no fogging effect. TiO$_2$ coated ceramic beads for photocatalytic water purification is another significant development[12].

However, TABLE 2[14] summarizes the latest advancements made in the field of photocatalyst sensitized dye degradation while a comprehensive list of organic pollutants which have been successfully photomineralized is summarized by Mills et. al.[15].

Kinetics of photomineralisation process

Identifying the key parameter in controlling the rate of photomineralisation of organic pollutants is a current source of debate. However, several factors have become significant in investigating the kinetics of photodegradation reactions sensitized by TiO$_2$, such as:

(i) crystalline form and concentration of TiO$_2$ particles; (ii) role of dissolved oxygen; (iii) nature and concentration of organic substrates; (iv) intensity of the illuminating source; (v) temperature and pH of the polluted medium; (vi) the presence of anions or interfering adsorbing species and (vii) the effect of mass transport. The general finding is that the initial rate of photocatalytic degradation of pollutant 'S' matches the Langmuir-Hinshelwood (L−H) kinetic model[10]:

$$r_i = -\frac{d[S]_i}{dt} = \frac{k_S K_S [S]_i}{1 + K_S [S]_i} \tag{1}$$

where r_i is the initial disappearance rate of pollutant S, $[S]_i$ is the initial concentration of pollutant S, K_S is the Langmuir adsorption constant of 'S' on the TiO$_2$ surface and k_S is the proportionality constant providing a measure of the intrinsic reactivity of the photoactivated surface with S. The coefficient, k_S, is proportional to I_a^m, where I_a is the intensity of light (photons s^{-1}) and m is a power term having values of 0.5 and 1 at high and low intensity respectively. The coefficient, k_S, is also proportional to the fraction of O$_2$ adsorbed, θ_{O_2}, which

can be expressed by the following equation:

$$\theta_{O_2} = \frac{K_{O_2}[O_2]}{1 + K_{O_2}[O_2]} \qquad (2)$$

where K_{O_2} is the Langmuir adsorption coefficient for O_2, which seems to be non-competitively adsorbed on TiO_2 due to its exclusive adsorption at Ti^{III} sites; hydroxyl radicals and organic substrates are adsorbed at Ti^{IV}-lattice oxygen sites. Thus equation (2) can be expressed more completely as follows:

$$r_i = \frac{\gamma K_{O_2}[O_2]I_a^{\ m}K_S[S]_i}{(1 + K_{O_2}[O_2])(1 + K_S[S]_i)} \qquad (3)$$

where γ is a proportionality constant.

Usually, this normalised Langmuir-Hinshelwood rate law is fairly applicable for the TiO_2 suspended system where the surface kinetics become more important compared to mass transport effects. This rate law has also been considered to apply to an immobilised catalyst, assuming that the concentration of the pollutant close to

TABLE 2 : Photocatalyst mediated degradation of dye compounds

Type of catalyst used	Type of dye degraded / mineralized	Form of the catalyst applied
TiO_2 (Degussa P-25)	Methylene Blue	Suspension
TiO_2 (Degussa P-25)	Methylene Blue and Eosin Y	Incorporated with rice husk ash
ZnO	Direct Yellow 86	Deposited on glass beads
TiO_2 and ZnO with commercially activated carbon	Acid Blue 29, Congo Red	Suspension
TiO_2 (synthesized)	Methylene Blue, Rhodamine B, Methyl Red, Methyl Orange	Suspension
Ag doped TiO_2	Congo Red, Methyl Orange, Direct Red 80, Reactive Red 17, Direct Yellow 50, Solophenyl Red 3BL (SR), Coperoxon navy blue RL,	Suspension
TiO_2 (Degussa P-25)	Acid Blue 9, Acid Orange 7, Reactive Black 5, Reactive Black 19	Coating
TiO_2 (Degussa P-25)	Acid Red 18	Suspension
ZnO	Rhodamine B	Suspension
TiO_2 (Degussa P-25), ZnO, ZrO_2, WO_3, CdS	Reactive Yellow 17, Reactive Blue 4, Reactive Red 2	Thin film
ZnO	Coralene Red F3BS	Suspension
TiO_2	Congo Red	Composite
ZnO	Orange II	Screen printed on ceramic tiles
Co-doped TiO_2 nanotube	Methylene Blue	Slurry

the catalyst surface remains the same as that in the bulk solution, which is not appropriate if mass transport effects become a significant parameter in controlling the rate. Specifically, for supported catalysts, mass transport effects are more significant in controlling the degradation kinetics[10]

Photocatalysis in suspended and supported form

The application of photocatalytic technology is now well-established and widely used and a number of reactors have been developed for the successful implementation of this technology. The choice of the reactors to be developed mainly depends on the experimental condition and application. Usually the reactors are classified in to two types: (i) the reactors that use the catalyst in suspension form and (ii) the reactors which use the catalyst in immobilized form. But the debate still

continues in developing the reactors using the catalyst in suspended or immobilized form[16]. The main advantage of using the photocatalyst in dispersed or suspended form is its high efficiency due to the large surface area of catalyst available for reaction. On the negative side, the suspended TiO_2 process also provides some disadvantages:

i. It cannot provide quantitative control of reaction conditions at the catalyst - liquid interface.

ii. The concentration of the organic substrate is known only in terms of the bulk / initial concentration.

iii. It is difficult to define the surface condition of TiO_2.

iv. Intermediates may affect the purity of the catalyst.

v. Much of the light may be scattered by the colloidal TiO_2; and

vi. The separation and recycling of the catalyst after treatment is difficult.

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However, post-treatment removal/recovery of the catalyst is the imperative issue after photomineralisation of the wastes. Particularly, to scale up the photocatalytic process for industrial application, there is growing concern for the recovery of the catalyst. Pozzo et. al.[17] highlighted that the post treatment to separate the catalyst from treated water is difficult and not cost effective. In most bench-scale studies, simple centrifugation or filtration techniques are often applied to separate the catalysts. However, such centrifugation or filtration techniques are not feasible to remove or recover the catalyst at an industrial scale[18]. Consequently, researchers have paid their attention to develop immobilized photocatalytic approaches, since this offers a much easier solid-liquid separation stage. Advantages of the immobilised catalyst system include:
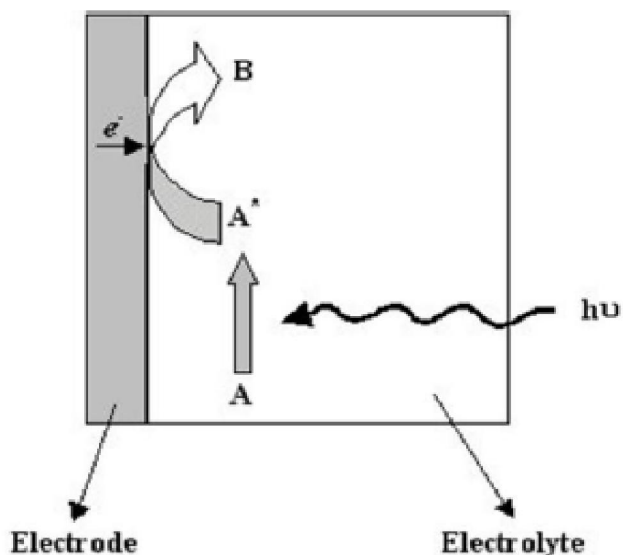
i. Surface detected - thus the reaction conditions at the semiconductor-solution interface are controlled.

ii. Continuous flow of the solution removes the catalyst from any type of contamination.

iii. The flowing solution effectively dissipates heat, so that the entire system can be operated under controlled temperature.
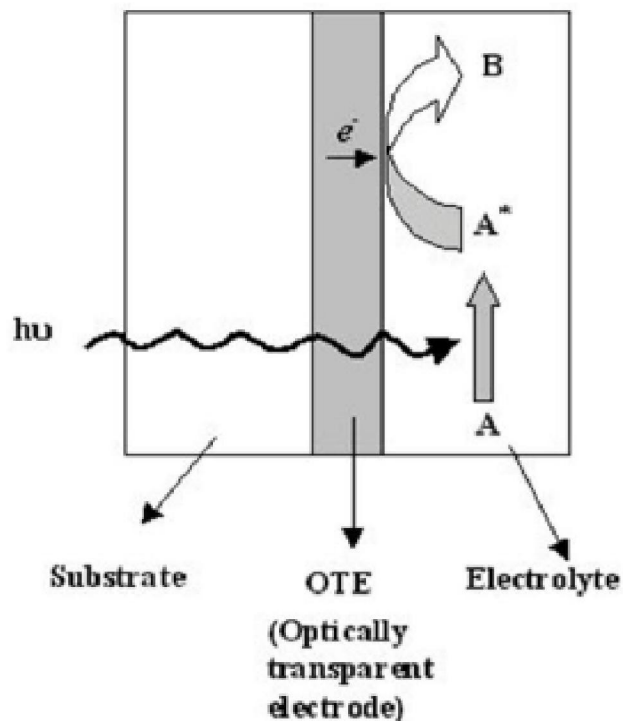
INTERFACIAL PHOTOELECTROCHEMICAL PROCESSES

The earliest demonstration of the semiconductor-liquid interfacial process was due to E. Becquerel in 1839[10]: a AgCl electrode, connected to a counter electrode in an electrochemical cell, exhibited a "photovoltaic effect" upon illumination, which is known as the "Bequerel effect". However, afterwards, a number of studies on the photoelectrochemistry of various semiconductor electrodes were rapidly followed up between 1955 and 1970[10], providing new insights on semiconductor-electrolyte interfacial processes. Specifically, during the 1960s, Gerischer[19] and Pleskov and co-workers[20-22] made a significant step forward to develop much of the theory of "semiconductor photoelectrochemistry."

Usually, the interfacial photoelectrochemical approach utilises a detector / indicator electrode as a potentiometric or amperometric probe to monitor the local course of the photochemical reactions. Several electrochemical devices have already been developed to

drive photoelectrochemical reactions through the front illumination or the back illumination as shown in Figure 3 (a and b respectively).

(a) Front illumination

(b) Back illumination

Figure 3 : Schematic diagram of front (a) and back (b) illumination driving a photoelectrochemical reaction

The pioneering work for the investigation of the electroassisted photolysis of water at an illuminated semiconductor electrode was successfully carried out by Fujishima and Honda in 1972[12]. They employed an

electrochemical cell containing a Pt black and a TiO_2 electrode, which were connected through an external bias. Due to the photoexcitation of the TiO_2 electrode, a passage of current from the Pt electrode to the TiO_2 electrode was observed and the photoinduced decomposition of water was monitored *via* the formation of O_2 and H_2 at the TiO_2 (illuminated) and Pt-electrodes respectively.

The channel flow method with electrochemical detection (CFMED) has already been used for studying the kinetics of photochemical reactions, initiating reaction by front (solution)-illumination[10]. Indeed, photoelectrochemical experiments should be conducted under regimes where mass transport is obviously controlled and quantified. From this point of view, the channel flow cell has been utilized as the basis of experimental methodology in photoelectrochemical systems and a number of photoelectrochemical studies have been carried out using the channel flow method with electrochemical detection[10,23-25]. The kinetics of Cl^- production from the UV-photocatalysed degradation of aqueous 4-chlorophenol (CP)[23,24] and oxygen reduction[25] by a thin TiO (Degussa P25) film, in both aerated and oxygenated solutions, have been determined by the channel flow method with electrochemical detection. The experimental approach allows surface kinetics and mass transport effects to be readily resolved.
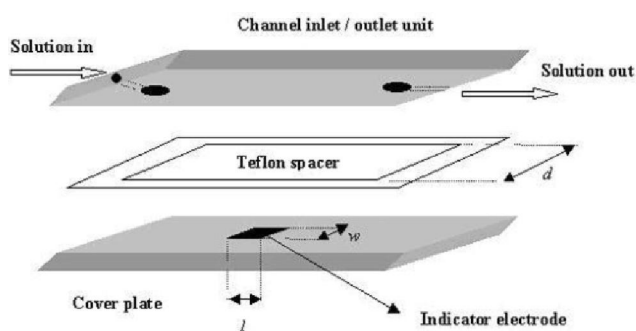

Figure 4 : Schematic of the channel flow cell employed for the investigation of interfacial

Scanning electrochemical microscopy (SECM) has also been used as a tool for investigating the interfacial photochemical processes under static condition using either the probes of localised[26] or broad illumination[27,28] of the surface. Both amperometric[29] and potentiometric[27] approaches have been utilised. Atomic force microscopy (AFM) has also been used to study interfacial photochemical processes focuding the TiO_2

- sensitized photomineralisation of partial and full monolayers of stearic acid[10].

A key point in mechanistic studies of photomineralisation processes concerns the role of oxygen. In the majority of cases, oxygen is employed as the electron scavenger. Since the quantum yields for photomineralisation under these conditions are low, the important questions are: (1) *what factors limit the efficiency of the photoprocess*? and (2) *does the rate of O_2 reduction govern the limiting step in the TiO_2-sensitised photooxidation of organic substrates*? To assess these questions, in particular, the likely important role of electron transfer (ET) to oxygen has been the focus of attention in theoretical and experimental studies under steady-state conditions[30-32], periodically illuminated systems[33] and electrochemically-assisted photocatalysis[34]. Theoretical models by Gerischer and Heller[30,31] led to the proposition that in particulate systems, electron transfer (ET) to oxygen could be slow. However, while there is experimental evidence for this[32] other investigations indicate that ET to oxygen is not rate limiting[35,36].

An interesting alternative approach to interpreting the kinetics of ET to O_2 was the application of a flux-matching condition by Lewis and co-workers[37] to describe the TiO_2 – catalysed photomineralisation of organic substrates. The overall rate of the interfacial process was considered to be predetermined by the fact that at steady-state, the flux of holes across the solid/liquid interface must be balanced by an equivalent flux of electrons. Using single crystal TiO_2 photoelectrodes, Lewis and co-workers determined the kinetics of O_2 reduction as a function of applied potential in the dark, and compared the cathodic rates of reaction to the photoanodic current characteristics in the absence of oxygen. The data successfully explained why recombination in TiO_2 – catalysed photomineralisation might be significant, but the authors also cautioned against extrapolating data obtained on TiO_2 single crystals to particulate systems.

Interfacial photochemical process is ultimately an *electrochemical process*, in which the anodic (photooxidation via h^+ consumption) and cathodic (photoreduction via e^- consumption) rates must balance. This correlation between anodic and cathodic routes of interfacial photochemical reaction has also been estab-

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lished[38,39] which provided new insights of the semiconductor mediated photocatalytic processes.

CONCLUSION

Semiconductor sensitized photocatalytic process has now emerged as an important area of research and considering the importance of interfacial photocatalytic processes, this feature article summarized and assessed the advances made in this area. Particularly different studies which have been carried out over the last two decades are discussed.

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