STUDY OF SEMICONDUCTOR PHOTOCATALYZED OXIDATION OF LACTIC ACID USED IN COSMETIC AND FOOD INDUSTRIES

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ABSTRACT

Photocatalysis has received enormous attention in recent years because of its potential application in environmental treatment and fine chemical synthesis. It is known under aqueous conditions, organic contaminants in wasted water can be degraded into CO_2 and H_2O, whereas under dry organic solvent or controlled pH, irradiation time, by using visible or UV light etc., the organic compounds may also be selectively oxidized into fine chemical products rather than complete mineralization[1-5]. Alpha hydroxy acids (like Lactic acid) is due to their excellent capability to penetrate skin, it is being used in a variety of skin care products and peeling agents including moisturizers, cleansers, eye cream, sunscreen and foundations etc., simultaneously the titanium oxide, zinc oxides etc. are used as the base for these materials. Hence, it is essential to understand that there may be photo-oxidation of lactic acid, which may cause other side effects on skin like irritation including redness, burning, itching, pain, scarring etc., by sensitized photo-oxidation of these skin care products in the presence of these semiconductors. Lactic acid is also being used as a food preservative, curing agent, wine taste enhancer and flavoring agent[6]. It is therefore, planed to investigate photo-oxidation of lactic acid by semiconductors. The produced photo-product has been isolated as its derivatives and then analyzed them by appropriate spectral or other suitable methods. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photo-products, where these are being used.

Key words: Glycolic acid, Titanium dioxide, Semiconductor, Photo-oxidation.

INTRODUCTION

Strong oxidation and reduction power of photo excited titanium oxide (TiO_2) was realized from the discovery of Honda-Fujishima effect. In 1972, Fujishima and Honda[7] reported photo induced decomposition of water on TiO_2 electrodes. Since Frank and Bard[8] first examined the possibilities of using TiO_2 to decompose cyanide in water, there has been an increasing interest in environmental applications.

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Photocatalysis has received enormous attention in recent years because of its potential application in environmental treatment and fine chemical synthesis. It is known under aqueous conditions, organic contaminants in wasted water can be degraded into CO_2 and H_2O, whereas under dry organic solvent or controlled pH, irradiation time, by using visible or UV light etc the organic compounds may also be selectively oxidized into fine chemical products rather than complete mineralization[1-5,9-11]. TiO_2 is the most frequently used photocatalyst because of its photo stability and low cost, combined with its biological and chemical inertness and resistant to photo and chemical corrosion. On the other hand, binary metal sulfide semiconductors such as CdS and PbS are regarded as insufficiently stable for catalysis and are toxic. ZnO is also unstable in illuminated aqueous solutions while WO_3 has been investigated as a potential photo catalyst, but it is generally less active catalytically than TiO_2. Many remarkable organic methodologies were developed in the last century, but toxic properties of many reagents and solvents were not known.

Alpha hydroxy acids (like Lactic acid) is due to their excellent capability to penetrate skin, it is being used in a variety of skin care products and peeling agents[6] including moisturizers, cleansers, eye cream, sunscreen and foundations etc., simultaneously the titanium oxide, zinc oxides etc. are used as the base for these materials. As a food additive it is approved for use in the EU[12], USA[13] and Australia and New Zealand[14]; it is listed by its INS number 270 or as E number E270. Lactic acid is used as a food preservative, curing agent, and flavoring agent[6]. It is an ingredient in processed foods and is used as a decontaminant during meat processing[15]. Lactic acid also is an alpha-hydroxy acid, used at 85%, pH 3.5 in hydroalcoholic solution, with activities similar to those of glycolic acid. It can be used as a peeling agent in the treatment of melasma. It is a low cost and easy to use product. The first pilot study was carried out by Sharquie et al., who showed that it was a safe and effective peeling agent for the treatment of melasma in dark skins[16,17].

There observed some side effects of lactic acid peels include prolonged redness, dryness, flakiness, irritation, hypersensitivity, itchiness, some swelling, especially with deeper peels, herpes activation with infection, hyper or hypopigmentation. The use of alpha hydroxy acid (i.e. lactic acid) can be able to reverse some of the damage caused by photo aging, but at the same time they make the skin more susceptible to photo aging. Several aspects concerning the mechanism of action of alpha hydroxy acids are still unknown. In particular, little is known about the correlation between the histopathology and functional changes in the stratum corneum induced by alpha hydroxy acids treatment[18,19], the only way to know for sure of the pH of such product is to test with pH strip. Paula Begoun has done this in her skin care product reviews found in her book "Don't go to the cosmetic counter without me." It is therefore planed to investigate photo-oxidation of lactic acid by

semiconductors. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used as cosmetic, wine and food industries.

EXPERIMENTAL

The organic compounds i.e. Lactic acid, Silica gel-G, Resublimed Iodine (sm), ninhydrene, titanium oxide, tungsten oxide, iron oxide, zinc oxide, cadmium sulphide, stannic oxide, copper oxide, some other semiconductors and other analytical chemicals. UV chamber with UV tube 30 W (Philips), spectrophotometer (Systronic), spectrometer (Systronic), tungsten filament lamps 2 x 200 W (Philips) for visible light, 450 W Hg-arc lamp, water shell to filter out IR radiations and to avoid any thermal reaction, necessary glass wares, thin layer chromatography and paper chromatography kits for to determine the progress of reaction, conductivity meter (Systronic) to determine the optimum yields of photoproducts, pH meter (Eutech pH 510), spectrophotometer (Systronic) and I.R. spectrometer (Perkin-Elmer Grating-377) was used.

The lactic acid solutions are prepared in water and acetonitrile solvent as the required concentrations as mentioned in the Table 1. The required concentration of semiconductor or mixed semiconductors has been added to the reaction mixture for heterogeneous photocatalytic reactions. Variations were made to obtain the optimum yield of photoproducts.

The progress of reaction was monitored by running thin layer chromatography at different time intervals, where silica gel-G was used as an adsorbent and ninhydrene or resublimed iodine (sm) chamber was used as eluent for spot test detection. For colorless spot detection a slide spot detector; UV chamber (Chino's) was used. At the end of reaction or the process the photoproducts has been isolated as its salts and by preparing appropriate derivatives were identified by spectrophotometer, IR-spectrometer, NMR-spectrometer. The optimum yield of obtained 2, 4-DNP [with 0.50 g and 84 mL HCl in 500 mL aqueous solution] was measured by using spectrophotometers and conductivity meter. Various probable variations like the role of different semiconductors, mixed semiconductors, visible and UV-light etc., was studied. Some sets of experiments are also made in controlled conditions such as in absence of UV or visible light, semiconductors and stirring etc.

RESULTS AND DISCUSSION

The effect of substrate

The effect of amount of substrate on the oxidation of lactic acid was studied at

different concentrations varying from 1.66×10^{-2} M to 5.55×10^{-2} M at fixed amount TiO_2 (1.66×10^{-2} M). The total volume of reaction mixture is 50 mL and the results are reported in the following Table 1 and shown in Fig. 1.

1. Solvent : Water

2. TiO_2 : 1.66×10^{-2} M (1.33 g/L)

3. Irradiation time : 120 min

4. Visible light : 2×200 W Tungsten lamps

Table 1: The effect of substrate

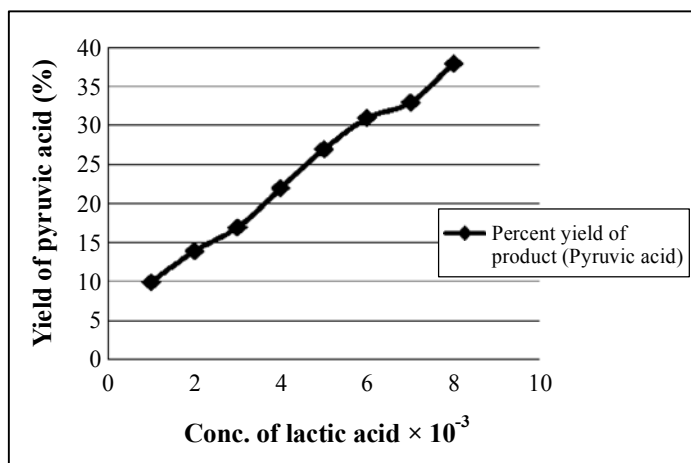| S. No.	Conc. of substrate (Lactic acid)	Percent yield of product (Pyruvic acid)
1	1.66×10^{-3} M	10%
2	2.22×10^{-3} M	14%
3	2.77×10^{-3} M	17%
4	3.33×10^{-3} M	22%
5	3.88×10^{-3} M	27%
6	4.44×10^{-3} M	31%
7	4.99×10^{-3} M	33%
8	5.55×10^{-3} M	38%

Fig. 1: The effect of lactic acid concentration

The effect of photocatalyst

Keeping all other factors identical the effect of amount of TiO_2 has also been observed. The total volume of reaction mixture is 50 mL and the results are reported in the following Table 2 and shown in Fig. 2.

1. Solvent   : Water

2. Lactic acid   : 3.33×10^{-2} M (3.00 g/L)

3. Irradiation time   : 120 min

Table 2: The effect of photocatalyst

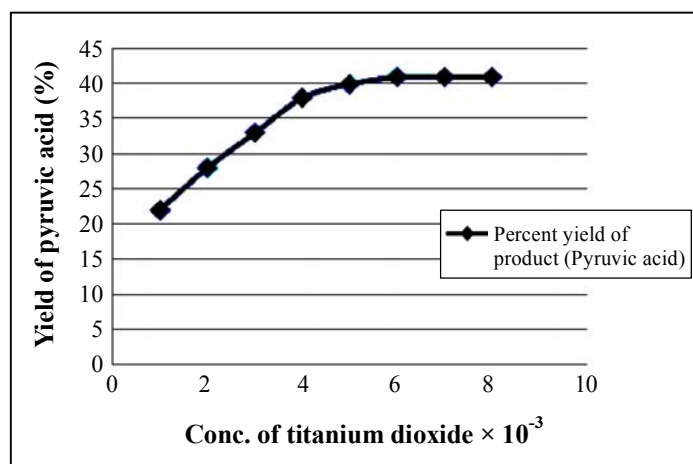| S. No.	Conc. of photocatalyst (TiO$_2$)	Percent yield of product (Pyruvic acid)
1	1.66×10^{-3} M	22%
2	2.50×10^{-3} M	28%
3	3.34×10^{-3} M	33%
4	4.18×10^{-3} M	38%
5	5.02×10^{-3} M	40%
6	5.85×10^{-3} M	41%
7	6.69×10^{-3} M	41%
8	7.53×10^{-3} M	41%

Fig. 2: Percent yield of product (Pyruvic acid)

The effect of type of radiations

   The effect of type of radiations on photocatalytic reaction was studied in visible light and ultraviolet light keeping all other factors identical. The total volume of reaction mixture is 50 mL and the results are reported in the following Table 3 and shown in Fig. 3.

1. Solvent : Water
2. TiO_2 : 1.66×10^{-2} M (1.33 g/L)
3. Irradiation time : 120 min
4. Visible light : 2×200 W Tungsten Lamps
5. UV Light: UV Chamber 30 W (Philips Tube)

Table 3: The effect of type of radiations

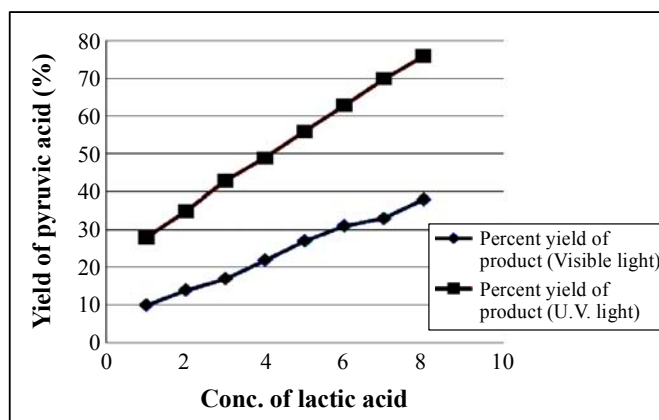| S. No.	Conc. of substrate (Lactic acid)	Percent yield of product (Visible light)	Percent yield of product (U.V. Light)
1	1.66×10^{-3} M	10%	28%
2	2.22×10^{-3} M	14%	35%
3	2.77×10^{-3} M	17%	43%
4	3.33×10^{-3} M	22%	49%
5	3.88×10^{-3} M	27%	56%
6	4.44×10^{-3} M	31%	63%
7	4.99×10^{-3} M	33%	70%
8	5.55×10^{-3} M	38%	76%

Fig. 3: The effect of light

The effect of nature of photocatalyst

The effect of the nature of photocatalyst on photocatalytic reaction was studied by different photocatalysts, which are Ferric oxide, Cadmium sulphide, Tungsten oxide, Titanium oxide, Stannic oxide and Zinc sulphide. The total volume of reaction mixture is 50 mL and the results are reported in the following Table 4 and shown in Fig. 4.

1. Solvent: Water

2. Lactic acid: 5.55×10^{-2} M (5.00 g/L)

3. Irradiation time: 180 min

4. Visible light: 2×200 W Tungsten lamps

Table 4: The effect of nature of photocatalyst

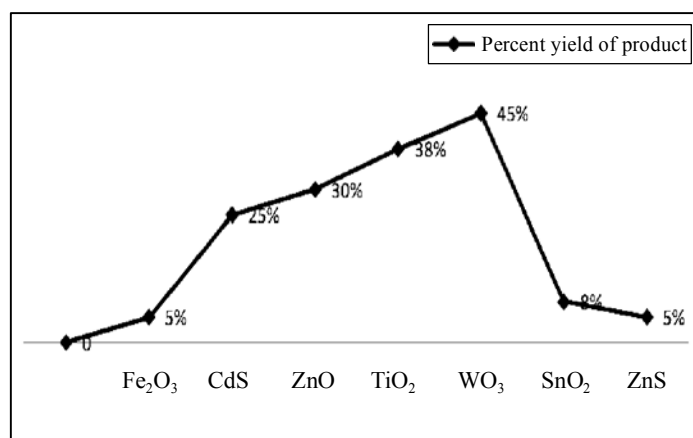| S. No.	Photocatalyst	Band gap (eV)	Wavelength (nm)	Percent yield of product
1	Fe_2O_3	2.2	564	5%
2	CdS	2.4	516	25%
3	ZnO	3.2	388	30%
4	TiO_2	3.1	400	38%
5	WO_3	2.6	477	45%
6	SnO_2	3.5	354	8%
7	ZnS	3.6	345	5%

Fig. 4: Percent yield of product

The effect of amount of on the oxidation of lactic acid was studied by using variable amount of substrate, as reported in Table 1 and Fig. 1. The highest efficiency was observed at optimum concentration. It may be explained on the basis that as the concentration of substrate increases, more substrate molecules are available for photocatalytic reaction and hence an enhancement on the rate was observed with increasing concentration of substrate.

The amount of photocatalyst on oxidation of lactic acid was investigated employing different concentrations of the TiO_2 as reported in Table 2 and Fig. 2. It was observed that the yield of photo-product increasing with increasing catalyst level up to 5.02×10^{-2} M and beyond this, the yield of photo-product is constant. This observation may be explained on the basis that on the initial stage, even a small addition of photocatalyst will increase the yield of photoproduct as the surface area of photocatalyst increases, but after a certain amount 5.02×10^{-2} M, addition of photocatalyst do not affect the yield of product because of the fact that at this limiting amount, the surface at the bottom of the reaction vessel become completely covered with photocatalyst. Now increase in the amount of photocatalyst will only increase the thickness of the layer at the bottom. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of lactic acid was studied by using different photocatalysts as shown in the Table 3 and Fig. 3. As we know that the low band gap is more suitable for visible light and this property quite resembles the observed data as the table reported.

Titanium dioxide (TiO_2) is the most common photocatalyst and comparably little research has been conducted on zinc oxide, ZnO, which could be a viable alternative for some applications. The effect of other semiconductor particle e.g. Fe_2O_3, CdS, WO_3 (having low band gap than TiO_2 semiconductor) on the TiO_2 catalyst photocatalytic reactions have also been studied. TiO_2 is the most frequently used photo catalyst because of its photo stability and low cost, combined with its biological and chemical inertness and resistant to photo and chemical corrosion. On the other hand, binary metal sulfide semiconductors such as CdS and PbS are regarded as insufficiently stable for catalysis and are toxic. ZnO is also unstable in illuminated aqueous solutions while WO_3 has been investigated as a potential photo catalyst, but it is generally less active catalytically than TiO_2. However, these can be combined with other semiconductors including TiO_2 to achieve greater photo catalytic efficiency or stability. Keeping all the factors identical the effect of the nature of photocatalyst on the photo-oxidation of lactic acid was studied by using different photocatalysts as shown in the Table 4 and Fig. 4.

It is now well established that the photocatalytic oxidation of several organic compounds by optically excited semiconductor oxides is thermodynamically allowed in

presence of oxygen at room temperature. On the basis of analytical, chemical and spectral data the product was characterized pyruvic acid.

After completion of photocatalytic reaction the photoproduct was characterized by usual qualitative tests treatment with (1) Semicarbeazide, (2) Hydroxylamine hydrochloride, (3) 2, 4-Dinitrophenyl phenyl hydrazones (M. Pt. 213°C) shows that photoproduct is pyruvic acid. IR analysis show two moderately intense peaks at 2903 cm^{-1} and 2892 cm^{-1} (C-H stretching) and peak at 1713 cm^{-1} (C=O stretching) confirms the presence of ketonic group in the 2,4-DNP of photoproduct. Absence of signal peaks at around 3200 cm^{-1} and at 1015-1050 cm^{-1} confirms the absence of alcoholic group in the 2, 4-DNP of photoproduct. The confirmatory test for lactic acid is carried out as following method:

Test for pyruvic acid

Since the general tests are employed to identify the pyruvic acid. Special test is done as follows:

To 0.5 mL of solution containing carbonyl acid + 0.5 mL water + 0.5 mL of 0.2% $FeCl_3.6H_2O$ + 3% of cysteine hydrochloride + 3 mL of 3N-HCl. The test tube is now immersed in a bath of ice and water, and 0.5 mL of freshly prepared 0.1% solution of alpha-methylindole is added. After being shaken, the tubes, still in bath, kept 24 hrs in to refrigerator. A light pink color appears which nearly reaches its maximal intensity in 24 hrs. Lactic acid gives orange color (480 nm). Optimum yield may be measured by optical density at 480 nm vs. time of irradiation.

Separation of 2, 4-DNP

A visible precipitate may or may not appear, according to the amount of hydrazone substances present. The whole is now shaken with 20 mL of ethyl acetate in a glass stopper 50 mL separating funnel. After separation, the aqueous layer, which is nearly colorless, is extracted with further 10 mL of ethyl acetate; as soon as the aqueous layer is colorless, as usually is the case after two extractions, it is discarded. The united ethyl acetate extracts now contain all the unchanged 2, 4-dinitrophenyl hydrazine together with the hydrazones which have been formed. The liquid is also acid, owing to the extraction of certain amount of hydrochloric acid; these must be neutralized by shaking with solid calcium carbonate (1, 2). The solution is decanted into a glass evaporating basin, washing the calcium carbonate with further ethyl acetate until it is colorless. The washing is added to the main bulk of fluid. The substances in solution must now be transferred to toluene (3). This is accomplished by evaporating the contents of the dish on a water bath to 1-2 mL and then, after removal from the bath, adding about 20 mL of toluene. The slightly cloudy yellow solution is again

transferred to the separating funnel and is thoroughly shaken with 5 mL of cold 25% sodium carbonate solution (4). If pyruvic acid was originally present its hydrazone dissolves in the aqueous layer, coloring it brown. This extraction is repeated with fresh Na_2CO_3 solution until the latter remains colorless; two or three repetitions usually sufficient. The united sodium carbonate layers are now acidified by adding concentrated HCl drop by drop. The 2, 4-DNP of pyruvic acid is precipitated and lemon-yellow suspension results. This extracted in a separating funnel with successive 10 mL portions of ethyl acetate until the aqueous layer is colorless (5). It is now usually to employ more than 20 mL of ethyl acetate to achieve this. The ethyl acetate solution now contains all the pyruvic acid hydrazone which was present, and is, evaporated to dryness in a glass basin on a water bath. The yellow residue is dissolved when cool in 5% alcoholic KOH (6), giving a deep red solution, which is made up in a graduated vessel with further alcoholic KOH to a volume such that the color is suitable for reading in colorimeter. In practice it is found that the total volume at this stage should be about 50 mL for every mg of pyruvic acid that was originally present in the reaction mixture.

(1)   If neutralization be omitted, the subsequent heating of the solution leads to the formation of small quantities of compounds other than the pyruvic acid derivative, which are extracted by the sodium carbonate, coloring it brown, and which are afterwards precipitated upon acidification, giving a reddish color in the final treatment with alcoholic potash. When the neutralization is properly carried out, the sodium carbonate always remains colorless in blank determinations, i.e. when no pyruvic acid is present.

(2)   It was that first the practice of neutralize the acid solution before extracting with ethyl acetate, but if this be done it is found that extraction has to be repeated a much larger number of times before the aqueous layer is colorless.

(3)   The solubility of pyruvic acid derivative in ethyl acetate is so great that it is not completely removed by sodium carbonate solution. Moreover, shaking the ethyl acetate solution with sodium carbonate solution to lead to a small amount of saponification, with the result that separation into layers is imperfect. The substitution of toluene for the ethyl acetate overcome both of these difficulties, but it cannot be used for extraction at the outset because the hydrazine and hydrazones are not sufficiently soluble in to render the process efficient.

(4)   The toluene extract and the sodium carbonate solution must both be at room temperature. Warm Na_2CO_3 react with other 2, 4-DNPs besides that of pyruvic acid.

(5)   A good deal of care must be taken at this stage that the effervescence produced by the librated CO_2 does not leads to loss by splashing.

Mechanism

On the basis of results and discussion the following tentative mechanistic part has discussed for photocatalytic oxidation of lactic acid, with collaborating the results already reported for other studied compounds.

With respect to a semiconductor oxide such as TiO_2, photocatalytic reactions are initiated by the absorption of illumination with energy equal to or greater than the band gap of the semiconductor. When the suspension of titanium oxide irradiated with visible light electron will be promoted from valence band to conduction band leaving a positive hole in the valence band:

$$TiO_2 + h\nu \rightarrow (h-e) \qquad \text{Excitation} \qquad …(1)$$

$$(h-e) \rightarrow h^+ + e^- \qquad …(2)$$

It was explained before, that the surface of TiO_2 with high surface area retains subsets of hydroxyls, where the net surface density is 4-5 hydroxyl per nm. In addition, suspension of TiO_2 in solution of lactic acid gives a surface hydroxide ion as locations for primary photo-oxidation processes. Photo holes are trapped by surface hydroxyl groups, whereas electrons are trapped by adsorbed oxygen:

$$h^+ + OH^-_{(s)} \rightarrow OH^\bullet \qquad …(3)$$

$$e^- + O_2\,(abs) \rightarrow O_2^{\bullet-}\,(abs) \qquad …(4)$$
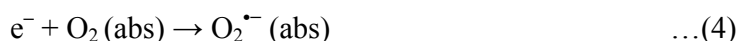
The formed radicals are reacted with adsorbed on the surface, is reacted with the formed water to regenerate hydroxyl group on the surface of the catalyst:

$$O_2^{\bullet-}\,(abs) + H_2O \rightarrow OH^-_{(s)} + OH_2^\bullet \qquad …(6)$$

Glyoxalic acid formed according the following steps:

$$CH_3\,CH^.(OH)COOH + OH_2^\bullet \rightarrow OHC\text{-}COOH + H_2O_2 \qquad …(7)$$

$$CH_3\,CH^.(OH)COOH + OH^\bullet \rightarrow OHC\text{-}COOH + H_2O \qquad …(8)$$

$$2\,CH_3\,CH^.(OH)COOH + \rightarrow CH_3C(O)COOH + CH_3\,CH_2\,(OH)COOH \qquad …(9)$$

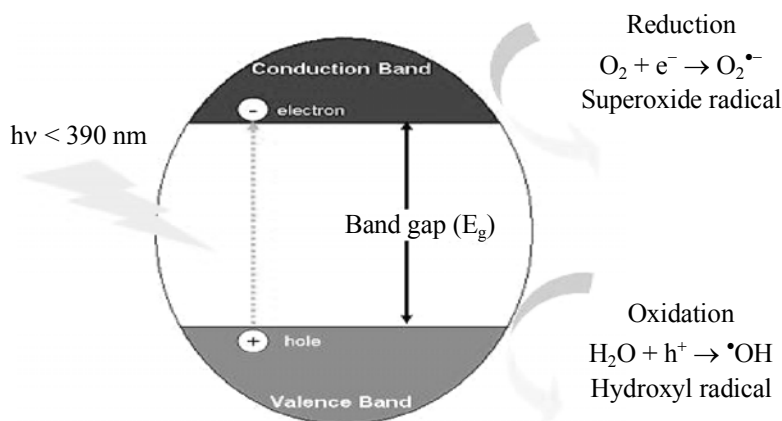The whole process can be summarized in the following Fig. 5.

Fig. 5

By the observations of photoproducts, it is very important to discuss the characteristic and nature (specially the toxic natures) of photoproduct as the photo reactants are being used in chemical peels, a variety of skin care products including moisturizers, cleansers, eye cream, sunscreen and foundations etc. The U.S. Food and Drug Administration permits up to1% TiO_2 as an inactive ingredient in food products. While there is no known health effects associated with the use of TiO_2, a recent study found that 3-6 year old children are the most affected group of people that consume TiO_2 particles from food products. So that the probable side effects of the photoproducts may be the common field of interest for the relevant researchers like dermatologists, pharmacists as well as the chemists. Similarly the side effects of food materials and wine-hangover may be due these type of oxidative products as the pyruvic acid may further oxidized into acetaldehyde which was traced in wine hangover cases. The mechanistic part of the photochemical transformations is also helpful for chemists to understand more about these new advanced oxidation processes. Hence, this part of reported work may help to arouse the interdisciplinary interest about the side effects of photoproducts, where these are being used.

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