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# STUDY OF SEMICONDUCTOR PHOTOCATALYZED OXIDATION OF GLYCOLIC ACID USED IN COSMETIC INDUSTRIES

**P. R. MEENA[*] and R. K. KHANDELWAL**

Department of Chemistry, M. L. V. Govt. College, BHILWARA (Raj.) INDIA

## ABSTRACT

The application of $TiO_2$ photocatalyst has mainly been focused on the decomposing toxic and hazardous organic pollutants in contaminated air and water, which is of great importance for the environmental protection. Glycolic acid is due to its excellent capability to penetrate skin, it is being used in a variety of skin care products 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 glycolic 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, due to presence of these semiconductors. It is therefore, planed to investigate photo-oxidation of glycolic 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

Titanium dioxide ($TiO_2$) has been intensively investigated as a semiconductor photocatalyst since Fujishima and Honda discovered the photocatalytic splitting of water on $TiO_2$ electrodes in 1972[1]. The ability of advanced oxidation technology to remove low levels of persistent organic pollutants as well as microorganisms in water has been widely demonstrated and, progressively, the technology is now being commercialized in many areas of the world including developing nations. Recently, the application of $TiO_2$ photocatalyst has mainly been focused on the decomposing toxic and hazardous organic pollutants in contaminated air and water, which is of great importance for the environmental protection[2-5].

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[*] Author for correspondence; E-mail: meenapushkarraj@gmail.com

Generally, two or more phases are involved in a photocatalytic reaction- a light source and a semiconductor material are used to initiate the photoreaction while the catalyst system can simultaneously carry out oxidation and reduction reactions using long wavelength, UV light as well as sunlight.

Glycolic acid is due to its excellent capability to penetrate skin it is being used in a variety of skin care products including moisturizers, cleansers, eye cream, sunscreen and foundations etc.; simultaneously the titanium oxide, zinc oxides etc are used as the base for these materials[6-22]. Hence, it is essential to understand that there may be photo-oxidation of glycolic 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 may be due to presence of these semiconductors. People with darker colored skin are at a higher risk of scarring pigment changes with alpha hydroxy acids. The use of alpha hydroxy acid (i.e. glycolic 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[23,24], 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 glycolic 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.

Inertness to chemical environment and long-term photo-stability has made $TiO_2$ an important material in many practical applications, and, in commercial products ranging from drugs to foods, cosmetics to catalysts, paints to pharmaceuticals, and sunscreens to solar cells in which $TiO_2$ is used as a desiccant, brightener, or reactive mediator.

## EXPERIMENTAL

The organic compounds i.e. Glycolic acid, Silica gel-G, Resublimed Iodine (sm), ninhydrene, titanium oxide, tungsten oxide, iron oxide, zinc oxide, cadmium sulphide, stannic oxide, copper oxide, uranyl acetate, some other semiconductors and other analytical chemicals.

UV chamber with UV tube 30 W (Philips), magnetic stirrer (Systronic), aerator for continues air bubbling, 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 glycolic acid solutions are prepared in water and methanol 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 was measured by using spectrophotometers and conductivity meter. Various probable variations like the role of different semiconductors, mixed semiconductors, uranyl ions, visible or UV-light etc., was studied. Some sets of experiments are also made in controlled conditions such as in absence of UV or visible light, air, semiconductors and stirring etc.

## RESULTS AND DISCUSSION

### The effect of substrate

The effect of amount of substrate on the oxidation of glycolic acid was studied at different concentrations varying from $1.63 \times 10^{-2}$ M to $4.89 \times 10^{-2}$ M at fixed amount $TiO_2$ ($1.63 \times 10^{-2}$ M). The total volume of reaction mixture is 50 mL and the results are reported in the following Table.

1. Solvent : Water
2. $TiO_2$ : $5.006 \times 10^{-2}$ M
3. Irradiation Time : 120 min
4. Visible Light : 2 × 200 W Tungsten Lamps

**Table 1**

| S. No. | Conc. of substrate (Glycolic acid) | Percent yield of product |
|---|---|---|
| **1** | $1.315 \times 10^{-2}$ M | 20 |
| **2** | $2.629 \times 10^{-2}$ M | 26 |
| **3** | $3.944 \times 10^{-2}$ M | 34 |
| **4** | $5.259 \times 10^{-2}$ M | 41 |
| **5** | $6.574 \times 10^{-2}$ M | 48 |
| **6** | $7.889 \times 10^{-2}$ M | 54 |
| **7** | $9.204 \times 10^{-2}$ M | 60 |

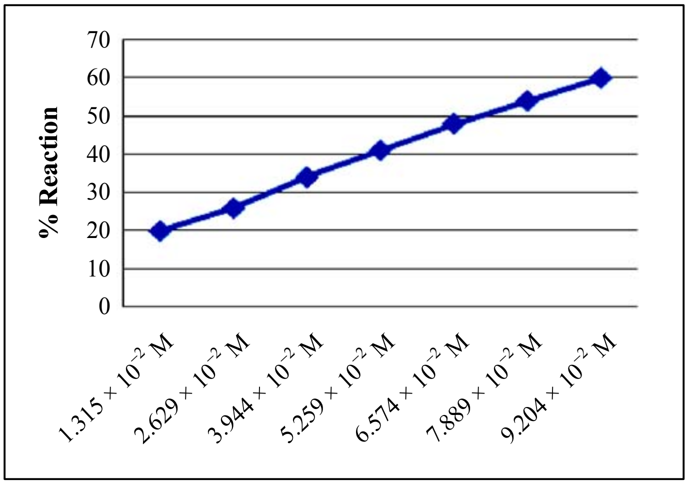

**Fig. 1: Effect of concentration of glycolic acid**

### 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.

1. Solvent : Water
2. Glycolic Acid : $5.259 \times 10^{-2}$ M

**Table 2**

| S. No. | Conc. of photocatalyst ($TiO_2$) | Percent yield of product |
|---|---|---|
| **1** | $1.251 \times 10^{-2}$ M | 15 |
| **2** | $2.503 \times 10^{-2}$ M | 32 |
| **3** | $3.754 \times 10^{-2}$ M | 44 |
| **4** | $5.006 \times 10^{-2}$ M | 60 |
| **5** | $6.257 \times 10^{-2}$ M | 48 |
| **6** | $7.509 \times 10^{-2}$ M | 34 |
| **7** | $8.760 \times 10^{-2}$ M | 18 |

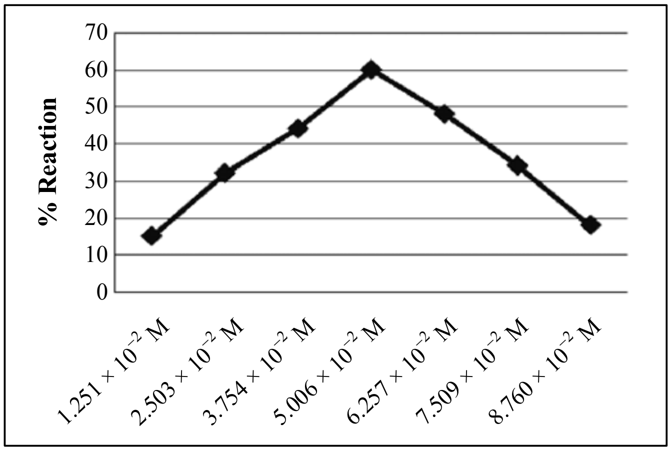

**Fig. 2: Effect of titanium oxide**

## 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.

1. Solvent : Water
2. Glycolic Acid : $5.259 \times 10^{-2}$M
3. Irradiation Time : 120 min.
4. Visible Light : 2 × 200 W Tungsten Lamps.

**Table 3**

| S. No. | Photocatalyst | Band gap (eV) | Wavelength (nm) | % Yield of product |
|---|---|---|---|---|
| 1 | $Fe_2O_3$ | 2.2 | 564 | 10 |
| 2 | CdS | 2.4 | 516 | 18 |
| 3 | $WO_3$ | 2.6 | 477 | 54 |
| 4 | $TiO_2$ | 3.1 | 400 | 60 |
| 5 | ZnO | 3.2 | 388 | 48 |
| 6 | $SnO_2$ | 3.5 | 354 | 34 |
| 7 | ZnS | 3.6 | 345 | 21 |

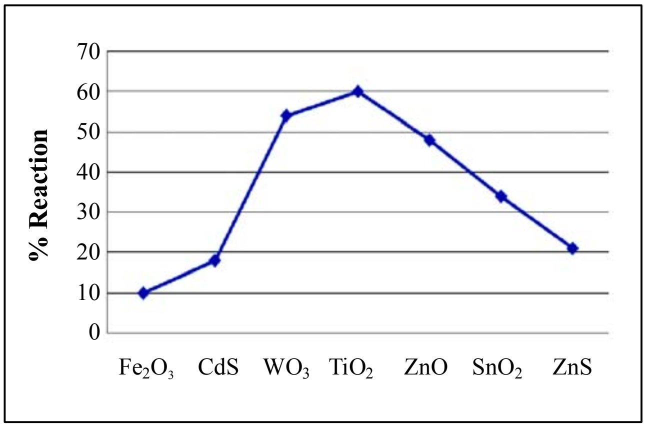

**Fig. 3: Effect of nature of semicoductors**

## The effect of uranyl ions

The effect of mixed photocatalyst on photocatalytic reaction was studied by using composite system $TiO_2$-$UO^{2+}$. The total volume of reaction mixture is 50 mL and the results are reported in the following Table.

1. Solvent : Water
2. $TiO_2$ : $5.00 \times 10^{-2}$ M
3. $UO^{2+}$ : $10.00 \times 10^{-4}$ M
4. Irradiation Time : 120 min.
5. Visible Light : 2 × 200 W Tungsten Lamps.

**Table 4**

| S. No. | Conc. of substrate (Glycolic acid) | Percent yield of product |
|---|---|---|
| 1 | $1.315 \times 10^{-2}$ M | 20 |
| 2 | $2.629 \times 10^{-2}$ M | 26 |
| 3 | $3.944 \times 10^{-2}$ M | 34 |
| 4 | $5.259 \times 10^{-2}$ M | 41 |
| 5 | $6.574 \times 10^{-2}$ M | 48 |

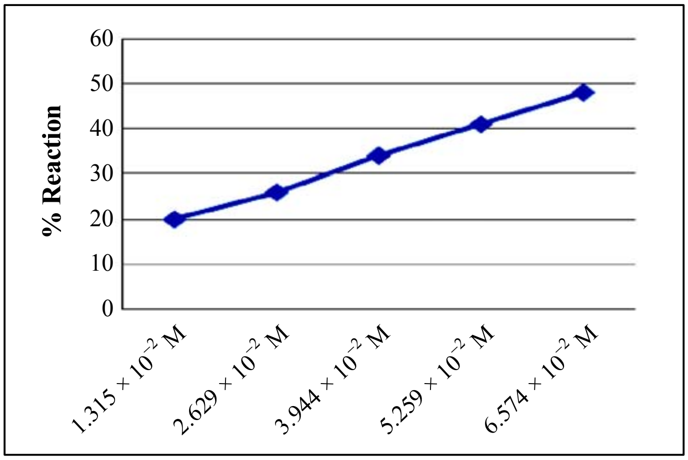

**Fig. 4: Effect of Uranyl ions**

The effect of amount of on the oxidation of glycolic 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 glycolic 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 $5.002 \times 10^{-2}$ 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 4.89 x $10^{-2}$ 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 glycolic 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.

The effect of mixed photocatalyst on photocatalytic reaction was studied by using composite system $TiO_2$-$UO^{2+}$ is recorded in Table 4 and Fig. 4. When we compare photocatalytic reaction of only with $TiO_2$ semiconductor and uranyl ions with $TiO_2$ semiconductor, results show that the presence of uranyl ion increases the rate of reaction potentially. Here U (VI) ion react with electron (which generated by excitation of $TiO_2$ semiconductor) and convert in U (V). Now this U (V) reacts with substrate molecule; Sukichi et al.[25] and $^{\bullet}OH$ radical, and converts it also in product; so the percent yield of product increases.

The effect of addition 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.

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 glyoxalic acid.

After completion of photocatalytic reaction the photoproduct was characterized by usual qualitative tests treatment with (1) Tollen's Reagent- silver mirror, (2) Schiff's Reagent- red violet color, (3) 2,4-Dinitrophenyl phenyl hydrazones ( M. Pt. 185°C) shows that photoproduct is glyoxalic acid. IR analysis show two moderately intense peaks at 3064 $cm^{-1}$ and 3030 $cm^{-1}$ (C-H stretching) and peak at 1693 $cm^{-1}$ (C=O stretching) confirms the presence of aldehydic 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 glyoxalic acid is carried out as following method:

## Test for glyoxalic acid

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 pink color appears, which nearly reaches its maximal intensity in 24 hrs. Glyoxalic 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. After filtering the reaction mixture the whole filtrate is now shaken with 20 mL of ethyl acetate in a glass stopper 100 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 of glyoxalic acid and hydrazones of other carbonyl compound, 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. 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. 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. If glyoxalic acid was originally present its hydrazone dissolves in the aqueous layer, coloring it brown. Here the hydrazones other than the glyoxalic acid left behind into the toluene. 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 glyoxalic acid is precipitated and orange- yellow suspension results. This extracted in a separating funnel with successive 10 mL portions of ethyl acetate until the aqueous layer is colorless. It is now usually to employ more than 20 mL of ethyl acetate to achieve this. The ethyl acetate solution now contains all the glyoxalic acid hydrazone, which was present, and is, evaporated to dryness in a glass basin on a water bath. In practice, it is found that the total volume at this stage should be about 50 mL for every mg of glyoxalic acid that was originally present in the reaction sample taken and the percentage of reaction has been calculated.

## Mechanism

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

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:

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

$$(\mathrm{h} - \mathrm{e}) \rightarrow \mathrm{h}^{+} + \mathrm{e}^{-} \qquad \ldots(2)$$

It was explained before, that the surface of $\mathrm{TiO_2}$ with high surface area retains subsets of hydroxyls, where the net surface density is 4-5 hydroxyl per nm. In addition, suspension of $\mathrm{TiO_2}$ in solution of glycolic 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:

$$\mathrm{h}^{+} + \mathrm{OH}^{-}_{\mathbf{(s)}} \rightarrow \mathrm{OH}^{\cdot} \qquad \ldots(3)$$

$$\mathrm{e}^{-} + \mathrm{O_2(abs)} \rightarrow \mathrm{O_2}^{\bullet -}\ \mathrm{(abs)} \qquad \ldots(4)$$

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:

$$\mathrm{OH}^{-}_{\mathbf{(s)}} + \mathrm{HO\ CH_2\ COOH} \rightarrow \mathrm{HO\ C^{\cdot}H\ COOH} + \mathrm{H_2O} \qquad \ldots(5)$$

$\mathrm{O_2}^{\cdot -}$, which adsorbed on the surface, is reacted with the formed water to regenerate hydroxyl group on the catalyst:

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

Glyoxalic acid formed according the following steps:

$$\mathrm{HO\ C^{\cdot}H\ COOH} + \mathrm{OH_2}^{\bullet} \rightarrow \mathrm{OHC\text{-}COOH} + \mathrm{H_2O_2} \qquad \ldots(7)$$

$$\mathrm{HO\ C^{\cdot}H\ COOH} + \mathrm{OH}^{\bullet} \rightarrow \mathrm{OHC\text{-}COOH} + \mathrm{H_2O} \qquad \ldots(8)$$

$$\text{2 HO C}^{\cdot}\text{H COOH} + \rightarrow \text{OHC-COOH} + \text{HO CH}_2\text{ COOH} \qquad \text{...(9)}$$

In presence urnyl ions the mechanism of reaction may be as follows:

$$\text{U(V)} + e^{-} \rightarrow \text{U(V)} \qquad \text{...(10)}$$

$$\text{U(VI)} + \text{HO CH}_2\text{ COOH} + \text{OH}_2^{\bullet} \rightarrow \text{U(IV)} + \text{HO C}^{\cdot}\text{H COOH} + \text{H}_2\text{O} \qquad \text{...(11)}$$

$$\text{HO C}^{\cdot}\text{H COOH} + \text{OH}^{\bullet} \rightarrow \text{OHC-COOH} + \text{H}_2\text{O} \qquad \text{...(12)}$$

$$\text{2 U(V)} \rightarrow \text{U(VI)} + \text{U(IV)} \qquad \text{...(13)}$$

$$\text{2U(IV)} + \text{O}_2 \rightarrow \text{U(VI)} \qquad \text{...(14)}$$

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

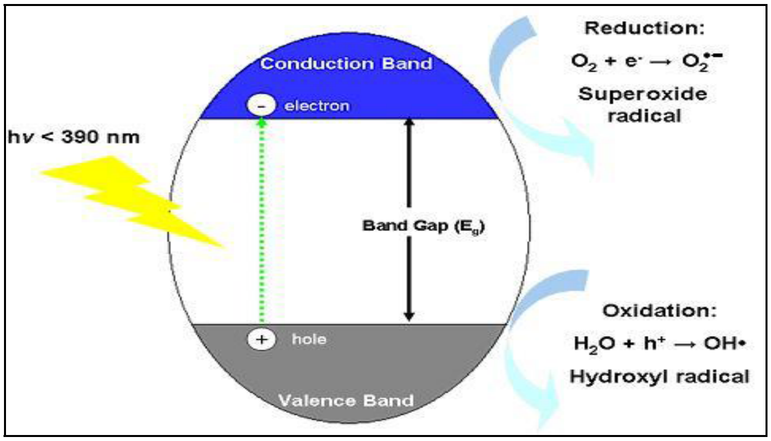

**Fig. 5**

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. 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. 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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