

# Article

# Effect of electron acceptors H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> on the generated reactive oxygen species <sup>1</sup>O<sub>2</sub> and OH<sup>•</sup> in TiO<sub>2</sub>-catalyzed photocatalytic oxidation of glycerol

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#### 1. Introduction

# ABSTRACT

The effect of the electron acceptors  $H_2O_2$  and  $O_2$  on the type of generated reactive oxygen species (ROS), and glycerol conversion and product distribution in the  $TiO_2$ -catalyzed photocatalytic oxidation of glycerol was studied at ambient conditions. In the absence of an electron acceptor, only HO<sup>•</sup> radicals were generated by irradiated UV light and  $TiO_2$ . However, in the presence of the two electron acceptors, both HO<sup>•</sup> radical and  $^1O_2$  were produced by irradiated UV light and  $TiO_2$  in different concentrations that depended on the concentration of the electron acceptor. The use of  $H_2O_2$  as an electron acceptor enhanced glycerol conversion more than  $O_2$ . The type of generated value-added compounds depended on the concentration of the generated ROS.

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Glycerol is a chemical that can be applied in various industries such as pharmaceutical, cosmetic, and food industries [1]. It is also a building block chemical that can be converted to high-valued chemical substances such as lactic acid [2–4], acrylic acid [5–7], dihydroxyacetone [8–11], acrolein [12–14], and propanedial [15] using processes such as hydrothermal [3,4], oxidation [5–7, 9–11], dehydration [12–14], and electrochemical treatment [8,15,16]. Photocatalytic oxidation is a process that can convert glycerol to various value-added compounds. Although various semiconductor metal oxides can be used in a photocatalytic reaction, including TiO<sub>2</sub>, ZnO, Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, ZrO<sub>2</sub>, CeO<sub>2</sub>, SnO<sub>2</sub>, Fe<sub>2</sub>O<sub>3</sub>, SrTiO<sub>3</sub> and BaTiO<sub>3</sub>, TiO<sub>2</sub> is the most widely used because of its high photocatalytic activity, stability, and suitable band gap energy [17]. Recently, it was reported that the use of  $TiO_2$  in either an anatase or rutile/anatase-rutile phase can enhance the partial photocatalytic oxidation of glycerol to dihydroxyacetone (DHA) and glyceraldehyde (GCD) to give selectivities of 4.5%-8% and 6.5%-13%, respectively [18]. It was also reported that a cylindrical photoreactor was more efficient than an annular photoreactor. The transformation of glycerol in the presence of  $TiO_2$  Degussa P25 was a function of the substrate concentration, and the generated products were derived from a direct electron transfer [19].  $TiO_2$  in the rutile phase with a high percentage of [110] facets enhanced glycerol conversion and achieved over 90% selectivity to hydroxyacetadehyde (HAA), while anatase with [001] or [101] facets gave only 16% and 49% selectivity for HAA, respectively [20].

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Nevertheless, the use of bare TiO<sub>2</sub> as a photocatalyst still gave a slow rate of glycerol conversion, probably due to the recombination of h+-e<sup>-</sup> that occurred after the charge separation when TiO<sub>2</sub> absorbed light with photon energy equal to or higher than its band gap energy. This caused a decrease in the photoinduced h+ [21]. Two strategies that can reduce this recombination problem are the use of a metal-doped TiO<sub>2</sub> photocatalyst and the use of an electron accepter. By using a metal-doped TiO<sub>2</sub>, it was reported that peroxide is the main oxidation product over irradiated aqueous Pt/TiO2 under conditions of glycerol photoreforming from two routes involving (1) the oxidation of surface hydroxyl groups by photogenerated holes and the subsequent dimerization of the so-formed hydroxyl radicals and (2) the consecutive reduction of surface-trapped oxygen by conduction band electrons [22]. A high production rate of the hydroxyl radical can enhance a high conversion of glycerol and product generation. A nanotube-structured TiO2 (TiNT) can enhance a conversion of glycerol to H<sub>2</sub> to twice that of nanoparticle TiO<sub>2</sub> (P25). The doping of TiNT with Pt and N (Pt-N-TiNT) can improve the activity for glycerol conversion up to 13 times compared with P25 [23]. The rate of the photoreforming of glycerol to H<sub>2</sub> and CO<sub>2</sub> was increased by a factor of 25 and 60, respectively, over  $Pt/TiO_2$  compared to the  $TiO_2$ photocatalyst, which was due to the increased separation of h+-e<sup>-</sup> pairs and the promotion of the rate limiting cathodic half reactions in the presence of metallic Pt [24].

To enhance glycerol conversion, the second strategy was carried out. It was reported that different types of ROS were produced in the presence of different electron acceptors as well as the TiO<sub>2</sub> phase. In the presence of H<sub>2</sub>O<sub>2</sub>, the rate of OH<sup>•</sup> formation increased for rutile and anatase mixed with rutile of 10%-20%, while pure anatase exhibited an opposite trend [25]. A higher production rate of  $O_2^-$  was observed with the TiO<sub>2</sub> in the anatase phase than that in the rutile phase. However, in the presence of  $O_2$ , a larger quantity of  $O_2^-$  was generated in the presence of  $TiO_2$  in the rutile phase compared with the anatase phase. The use of O<sub>2</sub> as an electron acceptor could facilitate the photoreforming of glycerol toward CO2 and H2 more than an un-metallized TiO<sub>2</sub>, while the activity was extremely high with the Pt/TiO<sub>2</sub> photocatalyst [24]. However, the final production of OH<sup>•</sup> and singlet oxygen (<sup>1</sup>O<sub>2</sub>), which are the main ROS that contribute to photodegradation, was more than one order of magnitude higher than  $O_2^{-}$ . [26]. The importance of the OH<sup>•</sup> radical is understandable because of its high oxidizing power. However, with other ROS species such as 102 and 02, very little work has been carried out to understand their formation in a photocataytic oxidation system. In addition,  $O_2^-$  can be quickly converted to <sup>1</sup>O<sub>2</sub> [26], resulting in its lower concentration in the photocatalytic system. <sup>1</sup>O<sub>2</sub> is a strong oxidation reagent for some organic compounds [27,28] due to its high quantum yield [25]. This suggests that it is an important species for the photocatalyic TiO<sub>2</sub> aqueous suspension [25-29].

In the present study, both  $H_2O_2$  and  $O_2$  were used as electron acceptors in the photocatalytic oxidation of glycerol with nanoparticle TiO<sub>2</sub>. The effects of these electron acceptors on the type of generated ROS (especially OH<sup>•</sup> and <sup>1</sup>O<sub>2</sub>), glycerol conversion, and product distribution were explored on the labora-

tory scale at ambient conditions. On addition, the reaction pathway for glycerol conversion via  $TiO_2$ -induced photocatalytic oxidation in the presence of  $H_2O_2$  and  $O_2$  as an electron acceptor was also proposed.

# 2. Experimental

# 2.1. Chemicals and catalyst

All chemicals used were analytical grade, including glycerol (GLY, 99.5%, QReC),  $H_2O_2$  (30 wt%, QReC),  $O_2$  (99.5% Praxair), DHA (98%, Merck), glyceric acid (GCA, 20 wt%, TCI), GCD (98%, Sigma Aldrich), glycoric acid (GCOA, 70 wt%, Ajax Finechem), formic acid (FMA, 98%, Merck), hydroxypyruvic acid (HPA,  $\geq$  95%, Sigma Aldrich), and formaldehyde (FMD, 37%, Merck). The photocatalyst used was commercial anatase TiO<sub>2</sub> powder (Sigma Aldrich). The probe compounds used to monitor the generation of the oxidizing species were *para*-chlorobenzoic acid (*p*CBA, Sigma Aldrich) and furfuryl alcohol (FFA, Sigma Aldrich).

#### 2.2. Characterization

The BET surface area of the utilized commercial TiO<sub>2</sub> was measured by N<sub>2</sub> adsorption by the Brunauer-Emmett-Teller (BET) technique with a surface area analyzer (Quantachrome, Autosorb-1). Its band gap energy was determined by a UV-Visible spectrophotometer (Shimadz UV-3600) in the wavelength range of 300–800 nm at room temperature. The bonding and valence state of the metals in the photocatalyst were determined using X-ray photoelectron spectroscopy (XPS, PHI 5000 VersaProbe II with monochromated Al  $K_{\alpha}$  radiation).

# 2.3. Glycerol oxidation

The conversion of commercial glycerol gave value-added compounds that included DHA, GCA, GCD, GCOA, FMA, HPA, and FMD, and was carried out in a hollow cylindrical glass reactor having a diameter of 10 cm. The reactor was placed in the middle of a UV-protected box with the dimensions of 0.68 m  $\times$  0.68 m  $\times$  0.78 m. A 120 W UV high pressure mercury lamp (RUV 533 BC, Holland) was placed on the roof of the UV-protected box as previously described [30].

In each experiment, 100 mL of glycerol (0.3 mol/L) was irradiated with UV light having the intensity of 4.7 mW/cm<sup>2</sup> and with a TiO<sub>2</sub> dosage of 3 g/L for 20 h. The solution was agitated continuously by a magnetic stirrer at 300 r/min to achieve complete mixing. Two types of electron acceptor including H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub> were used for their effect on glycerol conversion and product distribution. The feeding procedure of the two chemicals was slightly different due to their different chemical phases. The total required volume of H<sub>2</sub>O<sub>2</sub> (0.765 mL for 0.075 mol/L and 3.06 mL for 0.3 mol/L) was added into the glycerol solution prior to starting the reaction, while O<sub>2</sub> was fed continuously at a constant flow rate of 200 mL/min. As the experiment progressed, 2 mL samples were collected and quenched in an ice-water trap at 0 °C to terminate the reaction and then centrifuged on a KUBOTA KC-25 Digital Laboratory Centrifuge to separate the solid catalyst from the aqueous product.

The concentrations of glycerol and generated products were analyzed by a high performance liquid chromatography (HPLC) with a RID-10A refractive index detector (Agilent 1100). The stationary phase was Aminex HPX-87H ion exclusion (300 mm × 7.8 mm), and the mobile phase was a water-acetonitrile solution (65:35 *V/V*) with H<sub>2</sub>SO<sub>4</sub> (0.5 mmol/L) at a constant flow rate of 0.5 mL/min. Standard solutions of glycerol and expected major product compounds were used to identify the retention time and determine the relationship between the peak area and concentration.

The conversion of glycerol (X) and the yield of the monitored products (Y) of the photocatalytic oxidation were calculated based on carbon using Eqs. (1) and (2), respectively. The data reported were the average values obtained from at least three experiments and the error in this work was 3%.

$$X = \frac{\text{Moles of glycerol converted}}{\text{Total Moles of glycerol in reactant}} \times 100\%$$
(1)

$$Y = \frac{\text{Moles of glycerol converted to product } j}{\text{Total Moles of glycerol in reactant}} \times 100\%$$
 (2)

#### 2.4. Measurement of ROS

Both ROS, including the OH<sup>•</sup> radical and  ${}^{1}O_{2}$ , were determined by using specific scavengers. The production of the OH<sup>•</sup> radical was monitored by the loss of *p*CBA [31,32]. The production of  ${}^{1}O_{2}$  was monitored by the loss of FFA [32]. The concentration variation of *p*CBA and FFA was analyzed by HPLC equipped with a Pinnacle II C18 column (240 mm × 4.6 mm). The mobile phase was methanol-water-acetonitrile (55:35:10 *V*/*V*) with H<sub>2</sub>SO<sub>4</sub> (10 mmol/L) for *p*CBA detection. A 50/50 (*V*/*V*) solvent mixture of water-ethanol was used as the mobile phase for FFA determination. The 10 µL sample injected passed through the column with a constant flow rate of 0.5 mL/min.

#### 3. Results and discussion

#### 3.1. Catalyst characterization

The photocatalyst utilized was commercial TiO<sub>2</sub> having a BET surface area of 22.84 m<sup>2</sup>/g and particle size of less than 25 nm. Figure 1 exhibits the optical absorption spectra of TiO<sub>2</sub> recorded using a UV-visible spectrophotometer in the wavelength range of 300–800 nm at room temperature. A decrease of absorbance to a zero value was observed in the visible light region at wavelengths above 450 nm, showing its UV light absorption ability. By using the linear portion of the fundamental absorption edge of its spectra, the plot of  $(\alpha hv)^{1/n}$  against (hv) (inset of Fig. 1), where  $\alpha$  is the optical absorption coefficient determined from the obtained absorbance and hv is the energy of the incident photons, provided the value of the band bap energy (*E*<sub>g</sub>). The band gap energy of TiO<sub>2</sub> was 3.2 eV, which agreed with the theoretical band gap energy of anatase TiO<sub>2</sub>.

With regard to the bonding and valence state of Ti, as shown in Fig. 2, the XPS spectra of the  $TiO_2$  showed two symmetric



**Fig. 1.** UV-visible spectra and (inset) the dependence of  $(\alpha hv)^{1/2}$  on the photon energy of TiO<sub>2</sub> powder.

peak shape of Ti 2*p* assigned to the component of Ti 2*p*<sub>1/2</sub> and Ti 2*p*<sub>3/2</sub> at the binding energies of 465.2 and 459.4 eV, respectively, which confirmed the state of Ti as Ti<sup>4+</sup> in the TiO<sub>2</sub> structure. In the O 1*s* XPS spectra (insert of Fig. 2), the main O 1*s* peak appeared at the binding energies between 530.2–530.6 eV, 531.8–532.0 eV and 533.0 eV, assigned to the O 1*s* peaks characteristic of O<sup>2–</sup>, OH<sup>–</sup> and adsorbed H<sub>2</sub>O, respectively.

#### 3.2. Glycerol conversion and product distribution

To explore the effect of electron acceptor on the TiO<sub>2</sub>-induced photocatalytic oxidation of glycerol, two types of electron acceptors, H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, were utilized. A blank experiment was first carried out with the presence of either H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub>, but the absence of both UV light and TiO2. It was found that the presence of only H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> cannot facilitate the conversion of glycerol. However, the presence of irradiated UV light and TiO<sub>2</sub> in the absence of H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> promoted the conversion of glycerol to four value-added compounds, DHA, GCA, GCD and GCOA (Fig. 3(a)). The addition of  $H_2O_2$  into the irradiated UV light and TiO<sub>2</sub> system further enhanced the conversion of glycerol and gave one additional product, FMA (Fig. 3(b)). Using O2 as electron acceptor instead of H2O2 decreased the glycerol conversion to almost half (Fig. 3(c)). The glycerol conversion was about 50% at 20 h. The same three value-added compounds, DHA, GCD and GCOA, were still observed, while two more



Fig. 2. XPS spectra of the commercial TiO<sub>2</sub> powder.



Fig. 3. Photocatalytic conversion of glycerol (0.3 mol/L) and yield of products versus time over (a) UV light/TiO<sub>2</sub>, (b) UV light/TiO<sub>2</sub>/H<sub>2</sub>O<sub>2</sub> (0.3 mol/L) and (c) UV light/TiO<sub>2</sub>/O<sub>2</sub>.

compounds were generated in this system: HPA and FMD.

#### 3.3. Oxygen species

As previously reported, the oxidation of glycerol proceeded via the photogenerated oxidizing species, including photogenerated holes (h<sup>+</sup>) [33], H0<sup>•</sup> radical [34], and oxide radicals ( $^{1}O_2/O_2^{\bullet}$ ) [35] formed in the photo-cleavage of water and H<sub>2</sub>O<sub>2</sub> [22]. To monitor the type of ROS generated in the system in the presence of both H<sub>2</sub>O<sub>2</sub> and O<sub>2</sub>, parallel reactions were carried out to monitor the production of the two strong ROS, including the H0<sup>•</sup> radicals and  $^{1}O_2$ . The production of the former species was traced by the concentration loss of *p*CBA [31,32], while the generation of the latter species was monitored by the concentration loss of FFA [32]. More decrease of the *p*CBA and FFA concentrations indicated a higher generation rate of HO<sup>•</sup> radical and  $^{1}O_2$ , respectively.

As demonstrated in Fig. 4(a), under irradiated UV light and  $TiO_2$  and the absence of an electron acceptor, the concentration



Fig. 4. Variation of (a) pCBA and (b) FFA as a function of time in the irradiated UV light and TiO<sub>2</sub> system in the presence of  $H_2O_2$  and  $O_2$  as electron acceptors.

of *p*CBA decreased slightly as the reaction time increased, while that of FFA remained constant (Fig. 4(b)). This suggested the formation of HO<sup>•</sup> radicals in the irradiated UV light and TiO<sub>2</sub> system, but no <sup>1</sup>O<sub>2</sub>. When either H<sub>2</sub>O<sub>2</sub> or O<sub>2</sub> was used as an electron acceptor, the concentration of *p*CBA and FFA decreased significantly, suggesting the formation of both HO<sup>•</sup> radical and <sup>1</sup>O<sub>2</sub> in the system.

Based on the results and literature reports, the generation of HO<sup>•</sup> radicals and  ${}^{1}O_{2}$  in this study can be proposed as follows. When TiO<sub>2</sub> absorbed light having energy equal to or greater than its band gap energy ( $E_{bg}$ ), an electron (e<sup>-</sup>) is excited from the valence band into the conduction band, leaving a positive hole (h<sup>+</sup>) in the valence band according to Eq. (3) [22].

$$TiO_2 \xrightarrow{h\nu \ge E_{bg}} h^+ + e^-$$
(3)

In the absence of an electron acceptor, the photogenerated hole oxidized surface bonded water molecules to produce highly reactive OH<sup>•</sup> radicals, while the generated  $e^-$  can further react with proton (H<sup>+</sup>) to form gaseous H<sub>2</sub> according to Eqs. (4) and (5) [22,36,37].

$$h^{+} + H_2 O \rightarrow O H^{\bullet} + H^{+}$$

$$\tag{4}$$

$$e^- + H^+ \to 1/2H_2$$
 (5)

As exhibited in Fig. 4(a), a small quantity of OH<sup>•</sup> radicals was produced in this case, probably due to the recombination of  $h^+-e^-$  pairs, which usually occurred in the absence of an electron acceptor. This was confirmed by a low glycerol conversion and product yield as demonstrated in Fig. 3(a).

In the presence of an electron acceptor, *e.g.*  $H_2O_2$ , both OH<sup>•</sup> radicals and  ${}^{1}O_2$  were generated. Various elementary reactions can then proceed as follows. The  $H_2O_2$  can break down to form OH<sup>•</sup> radicals (Eq. (6)) when it absorbs UV light [38,39]. It can also react via the photogenerated electrons or photogenerated holes according to Eqs. (7) and (8) to form OH<sup>•</sup> radicals [40].

$$H_2O_2 \to OH^{\bullet} \tag{6}$$

$$H_2 U_2 + e^- \rightarrow H U + 0 H^2$$
(7)

$$H_2O_2 + h^+ \rightarrow 2OH^-$$
(8)

Furthermore, it can oxidize via the formed HO<sup>-</sup> and the photogenerated holes as well as the OH<sup>•</sup> radicals to form  $O_2^{\bullet-}$  radicals, which readily react with H<sub>2</sub>O<sub>2</sub> to form HO<sup>•</sup> radicals according to Eqs. (9)–(11), respectively [25,41]. Also, the generated  $O_2^{\bullet-}$  radicals can further react with h<sup>+</sup> and H<sup>+</sup> as well as H<sub>2</sub>O<sub>2</sub> to form <sup>1</sup>O<sub>2</sub> and HO<sup>•</sup> radicals as described above (Eqs.(12)–(14)). Both generated ROS have the ability to oxidize glycerol to form various products as shown in Fig. 3(b).

$$\begin{array}{l} H_2O_2 + 2HO^- + h^+ \to O_2^{\bullet-} + 2H_2O \\ H_2O_2 + OH^{\bullet} + HO^- \to O_2^{\bullet-} + 2H_2O \end{array}$$
(9) (10)

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^{\bullet} + HO^- + O_2 \qquad (11)$$

$$02^{\bullet-} + h^+ \rightarrow 102 \tag{12}$$

$$02^{\bullet-} + 02^{\bullet-} + 2H^+ \rightarrow H_2O_2 + 1O_2$$
 (13)

$$0_2^{\bullet-} + H_2 0_2 \rightarrow 10_2 + H0^- + 0H^{\bullet}$$
 (14)

Regarding the use of  $O_2$  as an electron acceptor, various possible reactions can be proposed. Initially, the supplied  $O_2$ can react with the photogenerated  $e^-$  to form  $O_2^{\bullet-}$  (Eq. (15)) and  $H_2O_2$  (Eq. (16)) [26, 36]. The generated  $O_2^{\bullet-}$  radicals can further react with h<sup>+</sup> and H<sup>+</sup> as well as  $H_2O_2$  to form  ${}^{1}O_2$  and HO<sup>•</sup> radicals (Eqs. (12)–(14)). Besides, the generated  $H_2O_2$  can dissociate after absorbing UV light or react with either photogenerated  $h^+$  or  $e^-$  to form OH<sup>•</sup> radicals according to Eqs. (9)–(11).

$$0_{2} + e^{-} \to 0_{2}^{\bullet-}$$
(15)  
$$0_{2} + 2e^{-} + 2H^{+} \to H_{2}O_{2}$$
(16)

The mechanism of glycerol conversion to value-added compounds under irradiated UV light and  $TiO_2$  in the absence and presence of  $H_2O_2$  has already been proposed in published work [30,43]. In brief, in the absence of  $H_2O_2$ , the photogenerated h<sup>+</sup> and the OH<sup>•</sup> radicals can attach to the 1°- or 2°- C atom of glycerol to form GCD or DHA, respectively [44]. Then, they can further oxidize the generated GCD to form GCA as well as cleave the C–C bond of GCA to form GCOA [45]. Our previous work demonstrated that DHA can be oxidized to GCA and GCOA [36]. High glycerol conversion and yield of value-added compounds were observed in the presence of  $H_2O_2$ , which was probably due to the large amounts of both OH<sup>•</sup> radical and  $^{1}O_2$  generated as well as their high oxidizing power.

In the presence of  $O_2$ , different value-added compounds were produced, particularly HPA and FMD. From the results, it seems that the type of generated ROS, including OH<sup>•</sup> radical and  ${}^{1}O_2$ , did not affect the types of value-added compounds produced from glycerol conversion because both species were produced when either  $H_2O_2$  or  $O_2$  was used as the electron acceptor. This difference was probably due to the difference in the ROS concentration produced in the system.

To prove this hypothesis, an additional experiment was carried out with a low  $H_2O_2$  concentration (0.075 mol/L). As demonstrated in Fig. 5, both OH<sup>•</sup> radical and  ${}^{1}O_2$  were still generated in the presence of both low and high  $H_2O_2$  concentrations but in different quantities as shown by the different decreases of *p*CBA and FFA concentrations. Large quantities of ROS were produced in the presence of a high  $H_2O_2$  concentration.

In the glycerol conversion and yield of value-added com-



**Fig. 5.** Variation of *p*CBA and FFA as a function of time in the presence of  $H_2O_2$  at different concentrations.



Fig. 6. Photocatalytic and catalytic conversion of glycerol (0.3 mol/L) and yield of products versus time in the presence of (a) UV light/ $TiO_2/H_2O_2$  (0.075 mol/L) and (b) UV light/ $TiO_2/H_2O_2$  (0.3 mol/L).

pounds produced at low  $H_2O_2$  concentrations (Fig. 6(a)), the types of value-added compounds was almost the same as those generated in the presence of a high  $H_2O_2$  concentration (Fig. 6(b)) but in low quantities except for FMA. Surprisingly, HPA was observed in this system, which indicated that the quantity of the ROS present affected the route of glycerol conversion as well as the type of generated products. In the presence of a low OH<sup>•</sup> radical quantity,  $1O_2$  probably was as the main ROS that attack the 1°-C atom of DHA to form HPA [46].

In any event, a glycerol conversion route can be proposed with the pathways possible for this system as demonstrated in Scheme 1. The threshold quantity of ROS that controls which route of glycerol conversion to form the different value-added compounds in the TiO<sub>2</sub>-catalyzed photocatalytic oxidation cannot be determined at this stage. More extensive and expanded studies will be carried out to determine the threshold quantity of the ROS. The results will be reported in the future.



**Scheme 1.** Proposed reaction pathways for glycerol conversion over  $TiO_2$  catalyst in the presence of  $H_2O_2$  and  $O_2$  as electron acceptors.

#### 4. Conclusions

Two types of chemical agents, namely,  $H_2O_2$  and  $O_2$ , were used as the electron acceptor for the photocatalytic oxidation of glycerol with TiO<sub>2</sub> at ambient conditions. HO<sup>•</sup> radicals were generated in the system having irradiated UV light and TiO<sub>2</sub> both in the absence and presence of an electron acceptor, while  $^{1}O_2$  can only be produced in the system with an electron acceptor. The use of both chemicals as the electron acceptor enhanced the generation of both OH<sup>•</sup> radicals and  $^{1}O_2$ . The types of product compounds were not affected by the type of ROS generated in the system but was affected by the ROS concentration. At least four compounds, namely, DHA, GCA, GCD, and GCOA, were produced in the photocatalytic oxidation of glycerol by TiO<sub>2</sub> in the presence of ROS in both low and high concentrations, while HPA and FMD were produced only at low ROS concentration.

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# **Graphical Abstract**

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# $\label{eq:entropy} \mbox{Effect of electron acceptors $H_2O_2$ and $O_2$ on the generated reactive oxygen species $^1O_2$ and $OH^{\bullet}$ in $TiO_2$-catalyzed photocatalytic oxidation of glycerol} \label{eq:entropy}$

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The effect of the electron acceptor ( $O_2$  or  $H_2O_2$ ) on the photocatalytic oxidation of glycerol by  $TiO_2$  was studied.  $H_2O_2$  enhanced the conversion of glycerol more than  $O_2$ . The type of generated compounds depended on the concentration of the formed ROS.

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