# Mechanistic aspect based on the role of reactive oxidizing species (ROS) in macroscopic level on the glycerol photooxidation over defected and defected-free TiO$_2$

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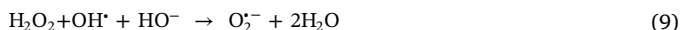
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## ARTICLE INFO

## ABSTRACT

The activity of commercial (defected-free) TiO$_2$ and black (defected) TiO$_2$ photocatalysts was comparatively tested in the glycerol photooxidation reaction. The preliminary results demonstrated that similar compounds, including glyceraldehyde (GCD), dihydroxyacetone (DHA), glycolic acid (GCOA), formaldehyde (FMD) and glycolaldehyde (GCAD), were generated from the photocatalytic oxidation of glycerol via both photocatalysts, but they differed in their yields. The black TiO$_2$ exhibited a higher photocatalytic activity to convert glycerol than the commercial TiO$_2$, due to the presence of some defective structure and its low band gap energy, and also promoted the generation of GCAD as the main product. In contrast, the commercial TiO$_2$ promoted the formation of GCD as the major product. The principle reactive oxidizing species (ROS) contributing for glycerol conversion via black TiO$_2$ can be ranked in the order of $O_2^{\bullet-} > {}^1O_2 > OH_b^{\bullet} > h^+/OH_s^{\bullet} > h^+$. The dominate ROS related to the conversion of glycerol to GCD and DHA were $O_2^{\bullet-}$ and $OH_b^{\bullet}$, respectively. The main ROS to alter GCD and DHA to GCAD/FMD was $O_2^{\bullet-}$, while the $h^+$ was the principle ROS to convert GCD to GCOA. Finally, the pathway of glycerol conversion and product distribution over black TiO$_2$ via various ROS in the presence of oxygen as electron acceptor is proposed.

## 1. Introduction

Photocatalysts accelerate chemical reactions after absorbing light quanta of the appropriate wavelength range depending on their band structure, which results in the excitation of electrons from the valence band to the conduction band of the photocatalyst and the formation of electron-hole ($e^- - h^+$) pairs [1]. Conduction band electrons are good reducing agents ($+0.5$ to $-1.5$ V/NHE), while the valence band holes ($h^+$) are a strong oxidizing agent [2]. Various kinds of semiconductors, including TiO$_2$, Fe$_2$O$_3$, WO$_3$, ZnO, CeO$_2$, CdS, Fe$_2$O$_3$, ZnS, MoO$_3$, ZrO$_2$, SiC and SnO$_2$, can be used as photocatalysts due to their narrow band gap and distinct electronic structure [3]. Among the above mentioned photocatalysts, titanium dioxide (TiO$_2$) has been more extensively studied due to its exceptional properties, such as a high refractive index and ultraviolet (UV) absorption, excellent incident photoelectric conversion efficiency and dielectric constant, good photocatalytic activity, high photo- and chemical-stability, and long-time corrosion resistance as well as nontoxicity [4,5]. However, the hands-on achievements of

TiO$_2$ are still hindered by its low quantum efficiency and ineffective operation in the solar spectrum. Therefore, various strategies have been addressed to modify TiO$_2$. In particular, in the last few decades, the introduction of defect disorder into the TiO$_2$ structure has received much attention for modulation of the physical and chemical properties of TiO$_2$ and its utilization in many applications, particularly in the field of photocatalysis [6,7].

Regarding to photocatalytic reaction mechanism, when TiO$_2$ photocatalyst is irradiated with light having a photon energy equal to or greater than its band gap energy (3.2 eV for anatase and 3.0 eV for rutile), the electrons ($e^-$) are excited from the valence band (VB) to the conduction band (CB), leaving behind the positively charged hole ($h^+$) in the valence band [8]. The photogenerated $h^+$ is able to oxidize the surface-bond water molecules to produce highly reactive hydroxyl radicals (OH$^{\bullet}$), while the photogenerated $e^-$ can readily react with a dissolved oxygen molecule to form superoxide radical ($O_2^{\bullet-}$), according to Eqs. (1) and (2) [9].
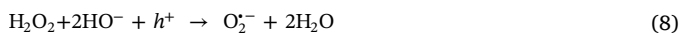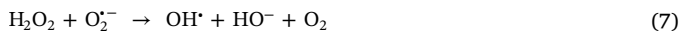
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$$h^+ + H_2O \rightarrow OH^\cdot + H^+ \tag{1}$$

$$O_2 + e^- \rightarrow O_2^{\bullet-} \tag{2}$$

$$O_2^{\bullet-} + e^- + 2H^+ \rightarrow H_2O_2 \tag{3}$$

$$O_2^{\bullet-} + h^+ \rightarrow {}^1O_2 \tag{4}$$

$$H_2O_2 \rightarrow 2OH^\cdot \tag{5}$$

$$H_2O_2 + e^- \rightarrow HO^- + OH^\cdot \tag{6}$$

$$H_2O_2 + O_2^{\bullet-} \rightarrow OH^\cdot + HO^- + O_2 \tag{7}$$

$$H_2O_2 + 2HO^- + h^+ \rightarrow O_2^{\bullet-} + 2H_2O \tag{8}$$

$$H_2O_2 + OH^\cdot + HO^- \rightarrow O_2^{\bullet-} + 2H_2O \tag{9}$$

The generated $O_2^{\bullet-}$ can further react with photogenerated $e^-$ or $h^+$ to form $H_2O_2$ or singlet oxygen ($^1O_2$), as shown in Eqs. (3) or (4), respectively. In addition, the generated $H_2O_2$ in this system can dissociate after absorbing UV light or react with either photogenerated $e$- or $O_2^{\bullet-}$ to form $OH^\cdot$ radicals, according to Eqs. (5) – (7). On the other hand, $H_2O_2$ can also be oxidized by photogenerated $h^+$ or reacted with $OH^\cdot$ as described in Eqs. (8) and (9) to form $O_2^{\bullet-}$ [9–12]. These generated ROSs, including $h^+$, $O_2^{\bullet-}$, $^1O_2$, $H_2O_2$ and $OH^\cdot$, are the dominate ROS that are responsible for the environmental purification and energy storage/conversion applications. Thus, the knowledge related to the role of the ROS involved in the photocatalytic process can help to understand and optimize the photocatalytic process.

Previously, it was reported that the oxidation of chlorinated hydrocarbons was controlled by the abstraction of H atom from the C–H bond via $OH^\cdot$ radicals [13]. The photocatalytic destruction of 6-hydroxymethyl uracil (6-HMU) under a UV irradiation was more pronounced in the presence of $Fe^{3+}$, $Cu^{2+}$ and humic acid, due to a high production level of $OH^\cdot$ in the process [14]. Under visible light activation, the degradation of N-nitrosodimethylamine (NDMA) on pure TiO$_2$ (Degussa P25) and surface-modified TiO$_2$ seemed to be mostly initiated by $OH^\cdot$ radicals [15]. Besides the participation of $OH^\cdot$ radical, another report showed that the $^1O_2$ was also generated through the photocatalytic process and it was main contribution for the degradation of NDMA [11]. The complete decolorization of an Acid Orange (AO7) was also achieved by the photocatalytic oxidation via aerated TiO$_2$ dispersion under visible light irradiation. The main ROS involved in the degradation of the AO7 was $O_2^{\bullet-}$ (or $HOO^\cdot$), while the $^1O_2$ was also active when it formed [16].

Within the above literatures and other recent published papers, there are still some contradictory results as to which primary ROS the photocatalytic reaction proceeds by, including $h^+$, $O_2^{\bullet-}$, $^1O_2$, $H_2O_2$ and $OH^\cdot$ [11,13–19]. It seems that the generation of the ROS in photocatalytic system depends on the catalyst morphologies (i.e. surface area, crystal phase and crystal size etc.), type of model compound as well as reaction conditions. So, the mechanistic information related to ROS of each organic compound should be thorough investigation.

In this study, glycerol was selected as a studied compound because it is a surplus compound which comes out as by-product from biodiesel production process. In addition, it possesses with high functionality molecule that can be converted to various high-value bio-based chemicals or materials [20]. Many researches have been conducted to convert glycerol to high value-added compounds ranging from biological to chemical catalytic routes [21]. Among the various catalytic routes, the glycerol conversion via photocatalytic route has been received much attention in a past few decades. However, the glycerol conversion over the photocatalytic process still requires thorough comprehension of the surface chemistry and reaction mechanism. The reaction pathways and type of generated value-added products can be varied with the reaction condition (catalyst type, light intensity, temperature etc.), reaction media (water with oxygen or hydrogen

peroxide) and the nature of catalyst surface (i.e. oxygen vacancies, surface defects). Thus, this work was firstly performed to investigate the role of ROS in macroscopic level on reaction pathway of glycerol conversion via photooxidation over defected-free and defected TiO$_2$. The knowledge obtained from this work may furnish a new insight into the conversion of glycerol to value-added compounds via the photocatalytic process and pave a new way to the rational design of TiO$_2$ based photocatalyst for selective photooxidation of glycerol.

## 2. Experimental

### 2.1. Preparation and characterization of photocatalysts

The two types of photocatalyst used in this work were commercial (defected-free) TiO$_2$ in pure anatase phase structure (Sigma Aldrich) and black (defected) TiO$_2$ prepared by the solution plasma process at a pulse frequency of 20 kHz and pulse width of 2.0 μs in 3.0 mM HNO$_3$. Details on the black TiO$_2$ photocatalyst preparation by innovative solution plasma process has been reported elsewhere [22]. The crystal structure and phase of both photocatalysts were analyzed by X-ray diffraction (XRD) using a Rigaku Smartlab (Rigaku) machine equipped with Cu Kα irradiation (λ = 1.54056 A$^o$). The chemical bonding states and valence band spectra of the synthesized sample were monitored by X-ray photoelectron spectroscopy (XPS) using a PHI 5000 VersaProbeII equipment and an Al Kα monochromatic X-ray source ($h\nu$ = 1486.6 eV). The unpaired spin electron was detected from the electron paramagnetic resonance (EPR) spectroscopy, recorded at room temperature on a JES-FA200 ESR spectrometer (JEOL) under a microwave power of 1 mW with a frequency of 9.44 GHz. The magnetic field was calibrated using the $g$-value of the $Mn^{2+}$ signal from a manganese (Mn) marker as the standard. The ultraviolet-visible (UV–vis) absorption spectra was detected by a UV–vis spectrophotometer (UV-3600; Shimadzu). The morphology of the TiO$_2$ photocatalyst was analyzed by transmission electron microscopy (TEM) using a JEM-2500SE (JEOL) instrument. The average diameter of a volume-based particle and size distribution were measured by dynamic light-scattering (DLS) using an ELS-7300 K (Otsuka electronics) photometer with a nominal measurable range of 0.5–10,000 nm.

### 2.2. Photocatalytic activity test

The photocatalytic activity of commercial TiO$_2$ and black TiO$_2$ was tested comparatively for glycerol conversion in a hollow cylindrical glass of 10 cm diameter, placed in a UV-protected box using a 120 W UV high-pressure mercury lamp (RUV 533 BCE, Holland) as the light source which can emit radiation in the range 200–600 nm. Prior to startup of the experiment, approximately 3.0 g/L of the selected photocatalyst was dispersed in 100 mL of 0.3 M glycerol solution (99.5%, QReC) under a constant agitation rate of 300 rpm to achieve a complete mixing. The system was bubbled with a constant flow rate of O$_2$ at 200 mL/min and held at this condition for 30 min to allow a uniform distribution and adsorption of glycerol and O$_2$ on the surface of the photocatalyst. Afterwards, the solution was irradiated with UV light at an intensity of 4.7 mW/cm$^2$ for 24 h. As the reaction progressed, 2 mL of sample was collected and then centrifuged on a KUBOTA KC-25 Digital Laboratory Centrifuge to separate the solid catalyst from the aqueous product. To trap the generated ROS during the photocatalytic reactions, 10 mM of the respective scavengers, including ammonium oxalate (AO; Sigma Aldrich), potassium iodide (KI; Ajax Finechem), isopropyl alcohol (IPA; QReC) furfuryl alcohol (FFA; Sigma Aldrich) and benzoquinone (BQ; Sigma Aldrich), was individually added into the glycerol solution before the photocatalytic activity test, for the elucidation of the different ROS role associated with photooxidation of glycerol and its intermediaries.

The concentration of glycerol and all generated products were analyzed by high performance liquid chromatography (HPLC) with a