

# Selective Oxidation of Glycerol Produces Valuable Products

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## Abstract

Under the situation of green economy, glycerol, as a polyol containing three hydroxyl groups, has high versatility and can be reacted to produce many different and more valuable fine chemicals and products. Glycerol is produced in large quantities in the process of biodiesel production, which is an important by-product of biodiesel production. Therefore, glycerol is considered as a potential platform chemical. Various value-added products of C3-C1 can be obtained by selective oxidation of glycerol via photocatalysis, electrocatalysis and photoelectrocatalysis, to improve the selectivity and yield of the resulting oxidation products. In this paper, the recent progress in the preparation of high value-added products by selective oxidation of glycerol in photocatalysis, electrocatalysis and photoelectrocatalysis is reviewed. The efficiency of various catalysts for glycerol conversion was emphasized. Various factors affecting the catalytic process were discussed. On this basis, the strategies for increasing the yield of glycerol, the limitations of existing catalysts and the future research directions are put forward. The mechanism of selective oxidation of glycerol by various catalytic methods is also discussed.

## Keywords

Glycerol, Selective Oxidation, Photocatalysis, Electrocatalysis, Photoelectrocatalysis, High Value-Added Product.

## 1. Introduction

### 1.1. Glycerin

In the 20th and 21st centuries, the chemical production of fossil fuels is the cornerstone of the development of modern society, providing many chemical products, but it has the potential energy shortage crisis, at the same time, increased dependence on fossil fuels will pose greater challenges to the ecological environment and sustainability<sup>[1]</sup>. At present, global warming caused mainly by CO<sub>2</sub> emission has received great attention, and countries have made corresponding policies. At COP28, the 198 parties to the UN Framework Convention on climate change 2023 a &quot; UAE consensus&quot; that global greenhouse gas emissions need to be reduced by 43% from 2019 levels, limit global warming to 1.5 °C and aim to triple renewable energy capacity and double energy efficiency globally by 2030. It also includes accelerating efforts to phase out undiminished coal-fired power and phase out inefficient fossil fuels. It also marks the beginning of the end of the fossil fuel era<sup>[2]</sup>. Therefore, under national policies, and in the context of the coming energy shortages and harmful effects on the environment, renewable material (biomass) fuels are seen as a promising alternative to fossil fuels, to meet energy needs and potentially reduce CO<sub>2</sub> emissions<sup>[3]</sup>.

Biodiesel production as a renewable fuel is growing steadily, and the OECD-FAO forecasts that it will remain high by 2025, although annual growth will level off<sup>[4]</sup>. International biofuel prices are expected to return to normal levels from their 2022 peak. Since then, biodiesel is expected

to increase slightly throughout the forecast period. The price of biofuels is determined by a number of fundamental factors, such as feedstock costs, crude oil prices, distribution costs and government policy [5].

Biodiesel is produced by an acid or base-catalyzed Transesterification of fats and oils (triglyceride) with methanol, producing a corresponding 3-mole FAME and 1-mole glycerol. This is equivalent to the production of about 100 kg of glycerol (about 110 kg of crude oil) from 1 ton of biodiesel,[6] as the rapid development of the biodiesel industry has led to a glut of glycerol,[7] and the price of glycerol on the market has fallen significantly. As a result, large amounts of glycerol are eventually incinerated for thermal energy production[8][9]. Taking into account, on the one hand, the low price of glycerol and its low cost as a raw material for the chemical industry, and, on the other hand, the fact that biomass is the only alternative to fossil fuels for the production of chemicals, so it makes more sense to turn glycerin into a value-added product. Therefore, better conversion of glycerol into value-added products under green conditions is conducive to stabilizing the price of glycerol and get great economic and environmental benefits.

## 1.2. Oxidation of Glycerol to High Value Chemicals

The early isolation of glycerol dates back to ancient times and was a by-product of the production of soap, (one of today's daily necessities). 1783, Carl Wilhelm Scheele in his experiments natural fats and oils were treated with alkalis, which were discovered academically and described as "A special sugar material", because it tasted sweet before it was named "Glycerin," from the Greek word "Glykos," meaning sweet, decades later<sup>[10]</sup>. Nevertheless, glycerin went unnoticed for a long time, until the production of nitroglycerin (the trinitrate of glycerin) in 1866. Nitroglycerin can form explosives when adsorbents and stabilizers are added. The state of glycerol synthesis production was maintained only for a short time<sup>[9]</sup> as a new trend emerged with the rapid growth of biodiesel production, which is considered to be a renewable fuel, it is accompanied by about 10% (by weight) glycerin as a by-product. Therefore, the production of glycerol is independent of its demand. As a result, the price of glycerol has fallen as a result of a severe surplus, and the glycerol waste stream from biodiesel plants has been burned even without any further use.

As a highly versatile molecule, glycerol is a polyol containing three hydroxyl groups, including two primary hydroxyl groups and one secondary hydroxyl group, such as alcohols, aldehydes, ketones, carboxylic acids, etc. . In 1994, the Lamy team made a pioneering contribution to the understanding of the glycerol oxidation pathway by chromatography the oxidation products of glycerol<sup>[11]</sup>. Since then, a large number of experiments have been carried out to investigate the mechanism of glycerol oxidation by different catalysts, but the whole mechanism has not been elucidated in published articles, only the more selective products <sup>[12][13]</sup>.

The product, glyceraldehyde (GLYD) , is formed by oxidation (2e-oxidation) of a primary-OH group and is an important organic chemical in the cosmetic industry and pharmaceutical manufacturing, starting materials in L-serine synthesis<sup>[14]</sup>, tanning agents in cosmetics, monomers in polymeric biomaterials <sup>[10]</sup> . 1,3-Dihydroxyacetone acid (DHA) is a product of oxidation at the secondary-OH group, and is widely used as a structural unit in the cosmetic industry and organic synthesis. The economic value of any product other than formic acid is higher than that of glycerin <sup>[15]</sup>. Table 1 summarizes several value-added compounds (US \$0.1/mL) that can be produced by glycerol oxidation, GLYD (US \$176.8/g), DHA (US \$1632.0/g), GLCA (US \$4.5/g), Tart (US \$9.6/g), and MESO (US \$25,000.0/g) were identified as the most important useful oxygenated compounds.

## 2. Glycerol Selective Photocatalytic Oxidation

Photocatalysis is a sustainable route for glycerol valorization, enabling redox reactions under ambient conditions using solar energy without extra chemical oxidants. It excels in tuning product selectivity via catalyst band structure, surface active sites and reactive oxygen species (ROS) regulation, which is critical for preserving glycerol's C3 skeleton to produce high-value partial oxidation products.

### 2.1. Mechanism of Selective Photocatalytic Glycerol Oxidation

The process initiates with semiconductor photoexcitation: photons with energy  $\geq$  band gap generate electron-hole ( $e^-h^+$ ) pairs. Valence band (VB) holes act as the primary oxidant to activate glycerol's hydroxyl groups, while conduction band (CB) electrons are captured by electron acceptors (typically dissolved  $O_2$ ) to generate ROS ( $O_2^{\bullet-}$ ,  $\bullet OH$ ,  $^1O_2$ ). The oxidation capacity of holes and ROS type directly govern reaction pathways.

Two core pathways are widely recognized:

**Selective partial oxidation (C3 pathway):** Dominated by direct hole oxidation or mild ROS ( $^1O_2$ ,  $O_2^{\bullet-}$ ), it selectively oxidizes primary/secondary hydroxyl groups without C-C bond cleavage, producing glyceraldehyde (GLYD), glyceric acid (GLCA) and high-value dihydroxyacetone (DHA). This is the primary design target of photocatalytic systems.<sup>[16]</sup>

**Over-oxidation and C-C cleavage (C2/C1 pathway):** Induced by non-selective  $\bullet OH$ , it breaks C-C bonds to form low-value C2/C1 products even  $CO_2$ , which is the main challenge for selective oxidation.

Key selectivity regulation strategies include: tuning semiconductor VB potential to match target hydroxyl oxidation, constructing specific surface active sites, controlling ROS generation, and optimizing reaction conditions.

### 2.2. Research Progress in Selective Photocatalytic Oxidation of Glycerol

Extensive studies have focused on developing efficient, selective and stable photocatalysts, with core systems summarized.

#### 2.2.1. $TiO_2$ -Based Photocatalysts

$TiO_2$  is the most widely studied photocatalyst for its low cost, stability and suitable band structure, but it suffers from only UV light response and severe glycerol over-oxidation caused by high VB potential.

Main modification strategies include: elemental doping (e.g., N doping) to extend visible light response and inhibit non-selective  $\bullet OH$  generation;<sup>[17]</sup> noble metal (Au, Pt, Pd) deposition to promote charge separation and construct specific active sites for targeted hydroxyl activation;<sup>[18]</sup> single-atom catalyst (SAC) modification to maximize atomic utilization and further improve DHA selectivity up to 83%.<sup>[19]</sup>

#### 2.2.2. Visible-Light-Responsive Semiconductor Photocatalysts

To improve solar utilization, various visible-light-responsive materials have been developed: Bismuth-based semiconductors ( $BiOCl$ ,  $BiVO_4$ )<sup>[20][21]</sup>: Defect engineering (e.g., oxygen vacancies) and carbon material modification are used to promote charge separation and achieve selective oxidation of primary hydroxyl groups.

Graphitic carbon nitride ( $g-C_3N_4$ )<sup>[22][23]</sup>: A metal-free polymer semiconductor, its performance is improved via nanostructure engineering, heteroatom doping and heterojunction construction to address severe  $e^-h^+$  recombination.

Metal-organic frameworks (MOFs)<sup>[24][25]</sup>: Their well-defined pore structure enables oriented confinement of glycerol molecules for selective hydroxyl activation, with Pt single atom modification further enhancing activity and GLCA selectivity.

### 2.2.3. Heterojunction Photocatalysts

Constructing matched band structure heterojunctions is an effective strategy to promote charge separation and tune redox capacity. Type II heterojunctions<sup>[26]</sup> (e.g., g-C<sub>3</sub>N<sub>4</sub>/BiOBr) significantly improve charge separation efficiency, while Z-scheme heterojunctions<sup>[27]</sup> (e.g., TiO<sub>2</sub>/WO<sub>3</sub>) retain strong redox capacity of both semiconductors while inhibiting non-selective •OH generation, achieving high C<sub>3</sub> product selectivity.

## 3. Selective Electrocatalytic Oxidation of Glycerol

Electrocatalytic oxidation of glycerol (EOG) is another promising green valorization route, driven by applied potential under ambient conditions. It offers higher conversion efficiency, flexible reaction control and easy scale-up compared with photocatalysis. Notably, EOG can be coupled with cathodic hydrogen evolution reaction (HER) to replace the sluggish oxygen evolution reaction (OER) in water electrolysis, simultaneously producing high-value chemicals at the anode and green hydrogen at the cathode with 30–40% reduced energy consumption.<sup>[28]</sup>

### 3.1. Mechanism of Selective Electrocatalytic Oxidation of Glycerol

EOG is a complex multi-electron transfer process, with pathway and product distribution governed by catalyst, applied potential, electrolyte pH and temperature. The core challenge is achieving high selectivity toward single C<sub>3</sub> products while avoiding C-C bond cleavage.

The reaction includes three key steps: glycerol adsorption on catalyst surface, stepwise deprotonation and electron transfer, and target product desorption or further oxidation/C-C cleavage. Adsorption strength of glycerol and intermediates directly determines the reaction pathway.

Alkaline electrolytes are most widely used for faster reaction kinetics, lower overpotential and higher selectivity. Two main C<sub>3</sub> oxidation pathways are recognized in alkaline conditions:

**Primary hydroxyl oxidation pathway:** Preferentially oxidizes primary hydroxyl groups to form GLYD, then rapidly to GLCA, and further to tartronic and mesoxalic acid, which is dominant on Au and Ag-based catalysts.

**Secondary hydroxyl oxidation pathway:** Selectively oxidizes secondary hydroxyl groups to form high-value DHA, which is more challenging and can be achieved on modified Pt and Pd-based catalysts.

C-C bond cleavage, the main side reaction, occurs at high potentials due to strongly adsorbed oxygen-containing intermediates attacking C-C bonds. It can be inhibited via catalyst electronic structure tuning and precise potential control.

### 3.2. Research Progress in Selective Electrocatalytic Oxidation of Glycerol

#### 3.2.1. Precious Metal-Based Electrocatalysts

Precious metal (Pt, Pd, Au, Ag) catalysts are widely studied for their high activity and tunable selectivity<sup>[29][33]</sup>.

**Au-based catalysts:** Unique resistance to C-C cleavage, achieving nearly 100% GLCA selectivity at low potentials, with alloying (e.g., AuCu) further improving activity while maintaining high selectivity.

**Pt-based catalysts:** Highest EOG activity, but pristine Pt suffers from severe C-C cleavage. Alloying with Bi, Pb and other metals blocks non-selective active sites, achieving DHA selectivity up to 91%.

**Pd-based catalysts:** Moderate activity and lower cost than Pt, with alloying (e.g., PdAu, PdNi) significantly improving C<sub>3</sub> product selectivity and reaction activity.

### 3.2.2. Non-Precious Metal-Based Electrocatalysts

To address the high cost of precious metals, low-cost non-precious metal catalysts have been developed, with Ni-based materials being the most promising. The in situ formed NiOOH on Ni-based catalyst surface is the active species for glycerol activation.<sup>[34]-[38]</sup>

Pristine Ni-based catalysts have high activity but poor selectivity, which can be optimized via element doping. NiFe layered double hydroxides (LDHs) achieve 78% GLCA selectivity and 92% glycerol conversion; NiCu LDHs show rare high DHA selectivity (up to 65%) on non-precious metal catalysts. Other Ni-based materials (Ni<sub>2</sub>P, oxygen vacancy-rich NiO) also show ultra-high EOG activity with low overpotential. Co, Cu and Fe-based catalysts are also studied, with Cu-based materials showing unique high selectivity toward valuable C<sub>2</sub> glycolic acid.

### 3.2.3. Coupling of EOG with Hydrogen Evolution

EOG-HER hybrid electrolysis systems significantly reduce energy consumption for hydrogen production. A system using NiFe LDHs anode and Pt/C cathode achieves 100 mA cm<sup>-2</sup> at only 1.39 V (420 mV lower than traditional water electrolysis), with 92% glycerol conversion, 78% GLCA selectivity and nearly 100% HER Faradaic efficiency. All-non-precious metal systems also show excellent long-term stability, demonstrating great industrial application potential.<sup>[39]</sup>

## 4. Glycerol Selective Photoelectrocatalytic Oxidation

Photoelectrocatalytic (PEC) oxidation integrates the advantages of photocatalysis and electrocatalysis. In a PEC system, a semiconductor photoanode generates e<sup>-</sup>-h<sup>+</sup> pairs under light irradiation, and an external bias drives electrons to the cathode for HER, nearly completely suppressing e<sup>-</sup>-h<sup>+</sup> recombination. Photogenerated holes on the photoanode drive glycerol oxidation. Compared with single photocatalysis/electrocatalysis, PEC oxidation achieves higher conversion efficiency, lower energy consumption and better product selectivity.

### 4.1. Mechanism of Selective Photoelectrocatalytic Glycerol Oxidation

The core process includes four steps: photoexcitation and e<sup>-</sup>-h<sup>+</sup> generation, charge separation and migration under external bias, glycerol oxidation by surface photogenerated holes, and cathodic reduction (typically HER). The synergistic effect of light excitation and applied bias enables efficient charge separation and tunable hole oxidation capacity, which is the key to regulating reaction pathway and product selectivity.<sup>[40]</sup>

Similar to the other two catalytic routes, the core challenge is inhibiting over-oxidation and C-C cleavage, which is achieved via band structure tuning, surface co-catalyst modification and reaction condition optimization.

### 4.2. Research Progress in Glycerol Selective Photoelectrocatalytic Oxidation

Efficient, stable and selective photoanodes are the core of PEC glycerol oxidation, with main systems summarized.

#### 4.2.1. TiO<sub>2</sub>-Based Photoanodes

TiO<sub>2</sub> is widely used for its high stability, but suffers from only UV response and non-selective oxidation. Modification strategies include elemental doping to extend visible light absorption, noble metal/SAC modification to promote charge separation and construct selective active sites (achieving DHA selectivity up to 85%), and heterojunction construction to further improve charge separation efficiency and C<sub>3</sub> product selectivity.<sup>[41][43]</sup>

#### 4.2.2. BiVO<sub>4</sub>-Based Photoanodes

BiVO<sub>4</sub> is a promising visible-light-responsive material with a narrow band gap (~2.4 eV), but suffers from severe charge recombination and slow surface reaction kinetics. Nanoporous structure design and co-catalyst (Co-Pi, FeOOH) loading significantly improve charge

separation and reaction activity, with dual co-catalyst modification achieving 78% glycerol conversion and 83% DHA selectivity. Heterojunction construction (e.g.,  $\text{WO}_3/\text{BiVO}_4$ ) further enhances photocurrent density and GLCA selectivity.[44][46]

#### 4.2.3. $\text{WO}_3$ -Based Photoanodes

$\text{WO}_3$  shows visible light response, high conductivity and acid stability, but its high VB potential causes non-selective oxidation. Surface modification with Pd/Au co-catalysts constructs specific active sites for targeted hydroxyl activation, achieving high DHA/GLCA selectivity, while heterojunction construction inhibits over-oxidation and improves charge separation.[47][48]

#### 4.2.4. PEC Hybrid Systems for Co-Production of Chemicals and Hydrogen

PEC glycerol oxidation can be coupled with HER to achieve simultaneous production of high-value chemicals and green hydrogen with ultra-low energy consumption. A Co-Pi/ $\text{BiVO}_4$  photoanode-based system achieves  $3.5 \text{ mA cm}^{-2}$  at only 0.6 V cell voltage, with excellent long-term stability. Tandem PEC systems even realize unassisted solar-driven glycerol oxidation and hydrogen production without external bias, providing a fully sustainable route for glycerol valorization.[49]

## 5. Challenges and Perspectives

Despite substantial progress, key challenges remain: low selectivity toward high-value C3 products, poor catalyst stability under harsh reaction conditions, ambiguous reaction mechanisms and intermediate identification, difficulty in lab-to-industrial scale-up, and lack of standardized evaluation protocols.

Future research directions should focus on: rational design of highly selective and stable catalysts; in-situ characterization techniques to reveal real-time reaction mechanisms; multi-catalysis integration to optimize conversion efficiency and selectivity; and development of continuous-flow reactors for practical industrial valorization.

## 6. Conclusion

Glycerol, an abundant low-cost by-product of biodiesel production, is a key biomass platform molecule. Selective oxidation via photocatalysis, electrocatalysis and photoelectrocatalysis provides sustainable green routes for converting glycerol into high-value chemicals such as DHA, GLYD and GLCA. This review summarizes the reaction mechanisms, catalyst design strategies and recent advances of the three catalytic routes. With further development of efficient catalysts and reaction systems, glycerol valorization will play an increasingly important role in the circular bioeconomy and sustainable chemical industry.

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