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# Electrochemical production of lactic acid from glycerol oxidation catalyzed by AuPt nanoparticles

Chencheng Dai [a,b], Libo Sun [b,f], Hanbin Liao [a], Bahareh Khezri [b,g], Richard D. Webster [b,g], Adrian C. Fisher [b,e], Zhichuan J. Xu [a,b,c,d,*]

[a] School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[b] The Cambridge Centre for Advanced Research and Education in Singapore, 1 CREATE way, Singapore 138602, Singapore
[c] Solar Fuels Laboratory, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[d] Energy Research Institute @ Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore
[e] Department of Chemical Engineering and Biotechnology, University of Cambridge, New Museum Site, Pembroke Street, Cambridge CB2 3RA, UK
[f] School of Chemical and Biomedical Engineering, Nanyang Technological University, 62 Nanyang Drive, Singapore 637459, Singapore
[g] Division of Chemistry & Biological Chemistry, School of Physical Mathematical Sciences, Nanyang Technological University, 21 Nanyang Link, Singapore 637371, Singapore

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ABSTRACT

The production of valuable chemicals from relatively inexpensive feedstocks utilizing electrochemical methods has been attracting widespread attention in recent years since it is highly efficient, decentralized, environmental-friendly and can operate in room temperature and pressure. Currently, the industrial production of lactic acid is mainly based on bio-fermentation, leading to drawbacks including severe conditions, unfriendliness to environment, low efficiency and requirement of expensive equipment, which can potentially overcome by electrochemical methods. Herein, we report for the first time the preparation of lactic acid at room temperature and pressure from the one-pot electro-oxidation of glycerol, a byproduct from biodiesel production. AuPt nanoparticles with different surface compositions were employed in this work to optimize the catalysis performance, and the glycerol oxidation was operated at a series of applied potentials, pH and glycerol concentration. The optimal lactic acid selectivity was 73%, obtained with Au-enriched surface at applied potential of 0.45 V vs. RHE.



## 1. Introduction

Lactic acid (LA) is a valuable chemical utilized for the production of biodegradable poly(lactic acid) (PLA), polyester, as well as a feedstock for the synthesis of green solvents and various commodity chemicals [1,2]. In addition, LA is widely used directly in the pharmaceutical, food and detergent industries [1,2]. Until now, the production of LA is mainly based on fermentation of carbon sources, which has several disadvantages, such as severe conditions, unfriendliness to environment and low efficiency [3,4]. The demand for LA has been estimated to grow yearly at 5–8% and been forecast to reach 367,300 metric tons by the year 2017[5]. One of the cheapest sources for LA is glycerol, a major byproduct from biomass conversion and soap manufacturing [6,7]. The global glycerol market size was 2.47 million tons in 2014 and is expected to increase 6.5% from 2015 to 2022 annually [8]. The market price of refinery glycerol (99.5%) is only approximately 500 USD/tons [9]. The production of LA from glycerol has been reported mainly using the hydrothermal [10–14] and hydrogenolysis methods, [15–17] with Au, Pt and their bimetallic catalysts frequently used for such methods [12–14,17]. Nevertheless, these methods typically suffer from severe drawbacks including requirement of expensive equipment and high energy input (such as high reaction temperature and pressure).

Electrochemical methods are often regarded as green processes because of their high energy efficiency in converting chemicals with electrons. Compared with the hydrothermal and hydrogenolysis methods, electrochemistry allows low reaction temperature and pressure due to the non-thermal activation in aqueous media. Additionally, the control of the applied potential, the solution pH, the glycerol concentration and the formulation of catalysts are expected to allow the tuning of the selectivity and activity of the oxidation reaction. The electrochemical oxidation of glycerol has been studied using a list of catalysts, such as Pt, Au, and a range of metals and metal oxides [18–25].

* Corresponding author at: School of Material Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, Singapore 639798, Singapore.
*E-mail address:* xuzc@ntu.edu.sg (Z.J. Xu).

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Pt is considered as the reference material for the electro-oxidation of alcohols in both acidic and alkaline media [18,23,24]. Kwon et al. [18] studied the mechanism and selectivity of glycerol oxidation on polycrystalline Pt employing an online measurement. They found that on Pt, glyceric acid (GLA) produced via oxidation of glyceraldehyde (GLAD) starting from 0.4 V vs. RHE was the main product in alkaline media, and as the pH was decreased GLAD became the main product. Other low concentration products also included dihydroxyacetone (DHA), hydroxypyruvic acid (HA), glycolic acid (GA), formic acid (FA), oxalic acid (OA), and tartronic acid (TA). Roquet et al. [24] studied the electro-oxidation of glycerol on platinum electrodes during long-term potential-controlled electrolysis. The product selectivity and conversion rate were found to depend greatly on the applied potential and on the pH of the electrolyte. They also found that in alkaline media the reaction kinetics were globally higher, and the adsorption and oxidation of glycerol with C—C bond cleavage appeared limited.

Au is inactive in acidic media for alcohol oxidation, while the surface becomes more active in alkaline media [18,23]. Kwon et al. [18] also studied the glycerol electro-oxidation on polycrystalline Au electrodes in alkaline media using an online method. They observed only three products, GA, FA and GLA. The GLA was detected first at 0.8 V vs. RHE instead of GLAD, which indicated the rapid oxidation from glycerol to GLA via glyceraldehyde, primarily due to the higher overpotential applicable to Au. This product was further oxidized at higher potential to form GA and FA. Wang et al. [21] prepared Au nanoparticles supported on extended poly(4-vinylpyridine) functionalized graphene. The products obtained from chronoamperometry at 0.2 V vs. Hg/HgO in alkaline media were mainly composed of GLA, with byproducts including FA, GA, OA and TA. Qi et al. [25] investigated the electro-oxidation of glycerol on Au in anion exchange membrane-direct glycerol fuel cells. Byproducts of the reaction after 12 h included mesoxalic acid (MA), GLA, GA, TA, OA with a minimal amount of LA (less than 10%). It should also be noted that during the preparation of this manuscript, Lam et al. reported the production of LA from glycerol electro-oxidation catalyzed by cobalt-based catalyst [26]. However, the highest selectivity towards LA is only 37% even in 3 M NaOH at 60 °C, and the selectivity towards LA is only 7% at room temperature. Regretfully, none of the reports on the electro-oxidation of glycerol have observed a major production of LA at room temperature and pressure using either online or offline measurement.

Herein, we report the electrochemical preparation of LA from glycerol at room temperature and pressure for the first time. AuPt bimetallic nanoparticles were prepared as catalysts. Since there has been no attempt to use AuPt for catalyzing the glycerol electro-oxidation so far, the AuPt synergetic effect on glycerol electro-oxidation was studied by comparing the performance of AuPt nanoparticles with different surface compositions and analyzing the corresponding oxidation products. Moreover, the influence of reaction parameters, including applied potential, glycerol concentration, solution pH, and reaction time, on the product selectivity, glycerol conversion and Faradaic efficiency was also investigated. Noticeably, different from the product compositions reported of glycerol oxidation on Au or Pt electrodes previously, the AuPt nanoparticles in this work exhibited LA selectivity as high as 73% under the optimal conditions.

## 2. Experimental details

### 2.1. Reagents

Dihydroxyacetone was purchased from Merck, glyceric acid was purchased from TCI, and all other chemicals were purchased from Sigma-Aldrich. All the chemicals were used without further purification. Solutions were prepared with deionized water and had resistivity no less than 18.2 MΩ·cm at 25 °C from Millipore Milli-Q.

### 2.2. Nanoparticle synthesis and electrode preparation

AuPt bimetallic nanoparticles were synthesized by modifying the method reported by Gaw et al. [27]. 0.25 mmol $HAuCl_4$ and 0.25 mmol $Pt(acac)_2$ were dissolved in 20 mL oleylamine. The solution was heated to 160 °C and maintained at this temperature for 2 h under argon blanket. Afterward, 100 mL ethanol was added and the mixture was centrifuged at 8000 rpm for 10 min. The resulted sediment was by the mixture of hexane and ethanol through centrifuging at 8000 rpm for 10 min for 3 times. The final sediment/nanoparticles was/were loaded to the Vulcan CX72 carbon support with a mass loading approximate 20 wt% by sonicating the mixture of nanoparticles and carbon in hexane in an ice bath for 3 h. The catalyst powders were then collected by purging Ar at room temperature and dried in vacuum. The catalyst ink (4 mg/ml) was prepared by mixing the catalyst with DI water/IPA/Nafion solution at a volume ratio of 4:1:0.2. The mixture was ultrasonicated in an ice bath for 1 h before dropped onto the carbon substrate.

### 2.3. Heat treatment of AuPt nanoparticles

The heat treatment of as-synthesized AuPt (90% $Pt_{surf}$)/C was carried out in a tube furnace (Lindberg/Blue M) using a quartz tube, and it followed the method reported by Suntivich et al. [28]. Three types of AuPt/C with different surface compositions were prepared. (1) AuPt/C with surface composition of 64% Pt: Approximately 40 mg AuPt (90% $Pt_{surf}$)/C was placed in a tube furnace, and purged with dry air at a flow rate of 100 mL/min. The tube furnace was heated up to 250 °C with a heating rate of 5 K/min, and maintained at this temperature for 30 min. Afterward, the tube furnace was allowed to naturally cool down to room temperature. (2) AuPt/C with surface composition of 29% Pt: Approximately 40 mg AuPt (90% $Pt_{surf}$)/C was placed in a tube furnace, and purged with dry air at a flow rate of 100 mL/min. The tube furnace was heated up to 250 °C with a heating rate of 5 K/min, and maintained at this temperature for 30 min. Then the dry air was replaced by argon with the same flow rate. The temperature was further raised up to 350 °C with the same heating rate, and the temperature was maintained for another 30 min. Afterward, the tube furnace was allowed to naturally cool down to room temperature. (3) AuPt/C with surface composition of 15% Pt: Approximately 40 mg AuPt (90% $Pt_{surf}$)/C was placed in a tube furnace, and purged with argon at a flow rate of 100 mL/min. The tube furnace was heated up to 500 °C with a heating rate of 5 K/min, and maintained at this temperature for 30 min. Afterward, the tube furnace was allowed to naturally cool down to room temperature.

### 2.4. Characterizations of AuPt nanoparticles

The surface composition was determined based on the electrochemical methods reported [27,28]. The electrochemical surface areas (ESAs) of Au and Pt in 0.5 M $H_2SO_4$ were measured by cyclic voltammetry utilizing a three-electrode system with a $Hg/Hg_2SO_4$ (sat. $K_2SO_4$) reference electrode and a graphite counter electrode, with Ar bubbling. The potential applied ranged from 0.05 V to 1.7 V vs. RHE at a scan rate of 50 mV/s. All electrochemical measurements were controlled by a PGSTAT30 Autolab potentiostat (Ecochemie). The particle size distribution was measured by a JEOL 2010 transmission electron microscope (TEM) at the operating voltage of 200 kV. Powder X-ray diffraction (PXRD) pattern measurements were recorded using a Shimadzu Thin Film X-ray