



# Influence of particle size on the electrocatalytic oxidation of glycerol over carbon-supported gold nanoparticles



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## ABSTRACT

The influence of gold particle size on glycerol oxidation was investigated using carbon-supported gold catalysts. Small gold particles of average diameter  $\leq 4.7$  nm had higher activities (on a mass basis) than medium-sized (14.7 nm) particles and were at least twice as active as catalysts containing large ( $\geq 43$  nm) gold particles. The small gold particles were also activated at lower potentials, resulting in lower onset potentials for glycerol oxidation. On the other hand, large gold particles had much higher onset potentials and were less stable during glycerol oxidation. While small gold particles were more active on a mass basis (primarily due to surface area effects), it was found that the specific activity (per unit real surface area) increased with increasing gold particle size. Based on evidence from Pb underpotential deposition experiments, it is proposed that this increase in specific activity can be related to an changes in the proportion of Au(111) and Au(110) surfaces as a function of particle size, with the Au(111) plane (dominant on large particles) having higher intrinsic activity compared to the Au(110) surface. This analysis also suggests that the lower onset potentials for glycerol oxidation on small nanoparticles can be attributed to the larger fraction of Au(110) facets at the surface of the small particles, and that the deactivation of larger particles is related to the high proportion of Au(111) facets on the surface of these particles. This analysis provides an important structural rationale for understanding the electrocatalytic behaviour of Au nanoparticles towards glycerol oxidation— independent of inherent size effects. As the important requirements for fuel cell catalysts are high mass activity, low overpotentials and high stability, our investigation demonstrates that all these conditions are met by the catalysts containing small gold particles defined by predominantly Au(110) facets.

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## 1. Introduction

Dwindling energy resources (such as oil and coal) and the need to cut down on emissions worldwide, have intensified efforts to identify new sources of clean, renewable energy. This naturally requires the development and/or improvement of technologies which could utilise such resources. One of the most promising solutions is fuel cell technology [1].

A typical fuel cell uses hydrogen as the fuel. However, organic alternatives to hydrogen are preferred as they are less dangerous to store and transport [2]. They are also advantageous in that they can be used in small, low-power fuel cells for electronic devices [3,4].

A number of alcohols have been studied with the purpose of replacing hydrogen in fuel cell applications. Of these, glycerol, a by-product of biodiesel production, is one very promising

alternative. Since biodiesel is currently the only viable alternative fuel to petroleum, its production has increased considerably in recent years [5]. This has resulted in an excess of glycerol by-product in the market, leading to a significant decrease in the price of crude glycerol. Other advantages to glycerol as a fuel option are its low flammability, low volatility, high boiling point and its renewable production from bio-feedstocks [6–8]. The drawback is that glycerol oxidation is slow, and its utilisation as a fuel therefore requires the development of efficient catalysts [9].

Gold has been shown to significantly outperform both platinum and palladium for glycerol oxidation in an alkaline medium, with peak current densities 6.5 and 8.8 times higher, respectively—although at much higher peak potentials [7]. However, we recently demonstrated that MnO<sub>2</sub>-modification of Au/C catalysts can lower the overpotential for activation of gold, giving lower glycerol onset- and peak- potentials and higher mass activities than unmodified Au/C [10]. We also demonstrated that the superiority of gold over platinum and palladium extends to the nano-scale, with all our catalysts displaying higher glycerol

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oxidation mass- and specific- activities than the nano- platinum and palladium catalysts reported in literature.

One of the questions that arose from our previous investigation was whether glycerol oxidation activities could be influenced by gold particle size. We now report the results of a systematic study into the effect of gold particle size on Au/C catalysts for glycerol electrooxidation.

## 2. Experimental

### 2.1. Preparation of gold colloids

#### 2.1.1. Reduction with $\text{NaBH}_4$

Gold colloids were synthesised using a modified method of Martin, *et al.* [11]. 6.1 ml of 0.05 M gold solution (from  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ , Sigma-Aldrich) in 0.05 M HCl was stirred into 280 ml water. This was followed by the addition, with rapid stirring, of 18.3 ml of 0.05 M  $\text{NaBH}_4$  in 0.05 M NaOH, to induce the formation of gold colloids.

#### 2.1.2. Reduction with tetrakis(hydroxymethyl)phosphonium chloride (THPC)

The method of Duff, *et al.* [12] was used as a basis for the preparation of gold colloids with THPC. To prepare the colloids, 231 ml water was added to a beaker, followed by the appropriate amounts of 0.2 M NaOH and 0.068 M THPC (from 80% THPC solution, Sigma-Aldrich). After 2 min, 10.2 ml of gold solution was added with rapid stirring. The gold concentration used was 0.025 M for small (<2 nm) colloids and 0.05 M for large colloids.

## 3. Reduction with Citrate

The gold: citrate molar ratios specified by Kimling, *et al.* [13] were used as a guideline for the preparation of size-controlled colloids. The colloids were prepared by adding 5.1 ml of 0.05 M gold solution in 0.05 M HCl to 249 ml water and then heating the solution to boiling. The required amount of trisodium citrate ( $\text{Na}_3\text{-cit}$ ) solution, which had been heated separately, was added to the gold solution and stirred vigorously while maintaining the temperature, until colloid formation was complete (3–10 min). The colloidal gold solution was then removed from heat and stirred until it reached ambient temperature.

### 3.1. Catalyst preparation

The carbon support (Vulcan XC-72R) was stirred in a small volume of water (minimum 20 ml) until fully wetted. The carbon dispersion was then added to the colloidal solution and the slurry was stirred for 20 h to ensure adequate time for gold deposition to occur. Thereafter, the catalyst was filtered and washed several times under filtration to remove any residual ions, and then dried at 60 °C overnight.

### 3.2. Characterisation

Powder X-ray diffraction (XRD) analysis of the catalysts was carried out at the Australian Synchrotron at a X-ray wavelength of 0.689 Å. The samples were loaded into 0.3 mm diameter capillaries (Special glass, Charles Supper Company Inc.) and diffraction data was obtained in the  $2\theta$  range of 8.2–88 degrees, using a Mythen detector. For some samples, small angle X-ray scattering (SAXS) data were collected using the SAXS/WAXS beamline at the Australian Synchrotron with a X-ray energy of 15 keV, a camera length of 900 mm and a Pilatus 1 M detector. Samples were measured in powder form, mounted in a plate between two pieces of

Scotch(TM) tape. Data collected for the tape (empty cell) and a blank carbon support were collected as a background. The background-subtracted data were fitted using the Irena 'Modeling II' macros [14]. The model used a Porod slope and constant as background parameters (to account for differences in the tape and supports), and a log-normal size distribution of dilute spheres (to model the Au particles). Wet chemical analysis of all filtrates and some solids was carried out to determine gold loadings. Catalyst samples were dissolved in *aqua regia* and analysed by atomic absorption spectroscopy (AAS). Dilute catalyst suspensions in isopropanol were deposited onto lacey carbon grids for analysis by transmission electron microscopy (TEM), using a Philips CM-200 operated at 200 kV.

### 3.3. Electrochemistry

For electrochemical testing, 5 mg of catalyst was weighed into a polypropylene test tube, followed by the addition of 1 ml of 0.5  $\text{mg ml}^{-1}$  Nafion in a 4:1 isopropanol (IPA): $\text{H}_2\text{O}$  solution. The catalyst/Nafion suspension was then diluted to 5 ml with 4:1 IPA: $\text{H}_2\text{O}$  solution, to yield a catalyst concentration of 1  $\text{mg ml}^{-1}$  and the suspension was ultrasonicated for 30 min to ensure good dispersion. A 10  $\mu\text{l}$  drop of catalyst suspension was then pipetted onto a polished (with 50 nm alumina) glassy carbon electrode plate over a hot-plate at 80 °C, and allowed to dry at that temperature for 1 min. For repeatability measurements, each catalyst was deposited and tested on 5 electrodes.

Electrochemical measurements were run in a standard 3-electrode PTFE cell using a Gamry Reference 600 potentiostat, a  $\sim 6 \text{ cm}^2$  platinum counter electrode and a Hg/HgO, 1 M KOH reference electrode. The electrodes were cycled five times between -0.9 and 0.8 V (vs. Hg/HgO) at 50  $\text{mV s}^{-1}$ , in order to clean the catalyst surface before electrochemical analysis. Cyclic voltammetry (CV) was carried out at 50  $\text{mV s}^{-1}$  in 1 M KOH (5 cycles) and at 10  $\text{mV s}^{-1}$  in 0.5 M glycerol/1 M KOH solution, in the potential range of -0.4 to 0.7 V. Potentiostatic measurements were carried out at both 0 and 0.2 V and EIS measurements were carried out at the same potentials in a frequency range of 1 MHz to 10 mHz.

Lead underpotential deposition (UPD) was used to identify the exposed low-index surface facets of the gold nanoparticles. Gold colloids were deposited directly onto a 3 mm glassy carbon electrode and allowed to dry. Prior to carrying out the lead UPD characterisation in a 1 mM  $\text{Pb}(\text{NO}_3)_2$ /0.1 M NaOH solution, the electrode was cleaned using the  $\text{PbO}_2$  deposition/dissolution technique [15], by cycling the electrode twice between -1 and 1 V (vs. SCE). Lead UPD characterisation was then carried out at 50  $\text{mV s}^{-1}$  between -0.2 and -0.75 V (vs. SCE).

## 4. Results and Discussion

A number of approaches were initially trialled in an attempt to obtain gold catalysts with varying average gold diameters ( $d_{\text{ave}}$ ): the utilisation of different reducing agents, altering the Au: reducing agent molar ratio and adjusting the gold loading on the catalysts. The preparation conditions, gold loadings and  $d_{\text{ave}}$  of each catalyst are listed in Table 1.

It has been shown that the average gold particle size can be increased by increasing the gold loading on the catalyst [16]. This was originally attempted using  $\text{NaBH}_4$  as a reducing agent and varying gold loadings from 1 to 20 wt % by simply changing the amount of carbon support added to the colloidal gold solution. However, while some variation in particle size was observed, with average diameters ranging from 3.9–5.7 nm, no trend was found relating particle size to gold loading. The method for synthesis of the gold nanoparticles used here, yields colloids with a particle size distribution (PSD) of 1.5–6 nm and an average size of 3.2 nm, which are

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