Electrochemical stability of carbon-supported gold nanoparticles in acidic electrolyte during cyclic voltammetry

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ABSTRACT

Cyclic voltammetry has been used to assess the electrochemical stability of gold nanoparticle-based electrocatalysts with differing initial particle size distributions in sulphuric acid electrolyte. The electrochemically active surface area (EASA), based on the gold oxide reduction charge, revealed that the electrocatalyst containing gold nanoparticles with an initial number-weighted average diameter of 4.5 nm was stable over 100 voltammetry cycles. Conversely, the electrocatalysts based on 3.1 nm and 2.9 nm gold nanoparticles showed a continuous decrease in the EASA in line with TEM and EXAFS data which confirmed growth of the gold particles during cycling. Importantly, we find no evidence to suggest that the nature of the stabilising ligand used during the gold nanoparticle synthesis, has any effect of the electrochemical stability of gold nanoparticles. When the anodic limit of the cyclic voltammograms was limited to below the gold oxide formation potential, the nanoparticles were stable, confirming that the loss in EASA is primarily related to the dissolution and growth of gold nanoparticles associated with the Au-AuO$_x$ redox process. Interestingly, an electrocatalyst initially containing 0.8 nm diameter gold nanoclusters had a surprisingly low EASA (these clusters appear not to exhibit normal Au-AuO$_x$ redox behaviour typical for the larger gold nanoparticles), but still showed significant particle growth during the cycling as confirmed by TEM and XPS analysis.

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1. Introduction

Gold nanoparticles have been proven as useful materials in a range of applications including, heterogeneous catalysis, electrocatalysis and sensing [1–6]. In heterogeneous catalysis, many authors have shown that gold nanoparticles are active catalysts for reactions such as CO oxidation [7,8], alcohol [9] and alkene oxidation [10–12]. Similarly, in electrocatalysis, gold based nanoparticles have been shown to be active for glycerol oxidation [13] and the electrochemical reduction of CO$_2$ to CO [14,15]. Furthermore, the addition of gold to platinum nanoparticles improves the stability of these nanoparticles during the oxygen reduction reaction in polymer electrolyte membrane fuel cells [16,17].

As gold is expensive, it is generally beneficial to utilise the gold in the form of nanoparticles to maximise the specific surface area for catalytic reactions. An additional advantage of this is that gold nanoparticles have unique size-dependent electronic properties as

they lose their metallic nature [18–22]. Also, the high fraction of atoms occupying corners and edges of nanoparticles can provide vacant sites for binding reactants and have strained Au-Au bonds, changing the behaviour of gold in catalytic reactions [23,24].

While gold nanoparticles have many advantages in catalytic processes, like all nanoparticles their small size can also lead to stability issues wherein a loss of specific surface area and their unique size-dependent properties can arise from dissolution and/or nanoparticle growth [25–29]. Of particular relevance is the Gibbs-Thomson effect, which predicts that nanoparticles should be less stable than the bulk material due to the changes in chemical potential brought about by the high curvature of the nanoparticle surface. This has been shown to strongly influence the dissolution of platinum nanoparticles with diameters of 2 nm or less [27]. Others have also shown that the anodic dissolution of platinum nanoparticles is strongly size dependent and follows a different mechanism to bulk platinum [28].

Surprisingly, despite the widespread interest in gold nanoparticle-based electrodes, to the best of our knowledge there is only one prior study concerned with electrochemical stability of gold nanoparticles [30]. In this previous paper it was revealed that the

stability of 12 nm gold nanoparticles was similar to bulk gold and that the citrate ligands used in the preparation of the nanoparticles did not prevent the oxidation of the gold. At anodic potentials of 1.37 V *vs.* SCE or above (in 0.01 M $HClO_4$) gold dissolution took place, and these dissolved gold species could be re-deposited once the potential was reduced, leading to the formation of larger nanoparticles. This anodic dissolution is consistent with previous work on bulk gold which is shown to occur in parallel with gold oxide formation at potentials above ∼1.3 V *vs.* RHE [17,31–34]. In addition, this anodic gold dissolution is pH dependent and differs in potentiodynamic vs potentiostatic measurements due to kinetic hindrance caused by the oxide layer which forms [34]. It has also been shown that gold dissolution occurs during the reduction of anodically formed gold oxide [17,32–35] and that this can dominate the dissolution process when the anodic potential used to form the oxide is limited to less than 1.6 V *vs.* RHE [17]. Given the importance of gold oxide formation in the dissolution of gold, the finding that gold nanoparticles may be easier to oxidise than bulk gold [36] will have implications for the electrochemical stability of gold nanoparticles.

The gold dissolution (and re-deposition of the dissolved gold species at reducing potentials) which can occur during cyclic voltammetry is frequently used to clean or pre-treat gold electrodes prior to other electrochemical measurements. Gold oxide reduction charge measurements from cyclic voltammetry are also often used to determine the electrochemically active surface area (EASA) [37,38], with this EASA enabling specific electrocatalytic activity (*i.e.* activity measurements independent of surface area) to be made. For bulk gold electrodes this pre-treatment approach is well established, however this is also applied to gold nanoparticle electrodes prior to examining their electrocatalytic activity [4,5,36,39–42]. Given that some gold dissolution will occur during this pre-treatment, it should be expected that changes to the particle size distribution will occur, thus making it difficult to establish structure- or size-based activity relationships based on initial nanoparticle morphology. Furthermore, if cyclic voltammetry is used to determine the EASA of nanoparticle electrodes, it must also be expected that the act of measurement will also alter the EASA itself.

Here, we evaluate the electrochemical stability of gold nanoparticles of various sizes during repetitive potential cycling by analysing changes in EASA together with TEM, XPS and EXAFS analysis to support the conclusions.

2. Experimental

Chemicals used include: gold(III) chloride trihydrate (99.9%, Sigma Aldrich), isopropanol (100%, ASCC), sulfuric acid (ACS grade, Ajax Finechem), Vulcan XC-72R (>99%, Cabot), dichloromethane (ACS grade, Merck) sodium borohydride (95%, BDH Chemicals Ltd.), hydrochloric acid (34-37%, Fisher Scientific), nitric acid (ACS grade, Merck), hexane (99 + %, Sigma Aldrich), 18.2 MΩ cm deionised (DI) water (Sartorius Arium 611UV), and dissolved Nafion (LIQUion EW1100, Ion Power, Inc.)

Gold nanoparticle suspensions were produced following methods described by Martin et al. [43] Duff et al. [44] and Weare
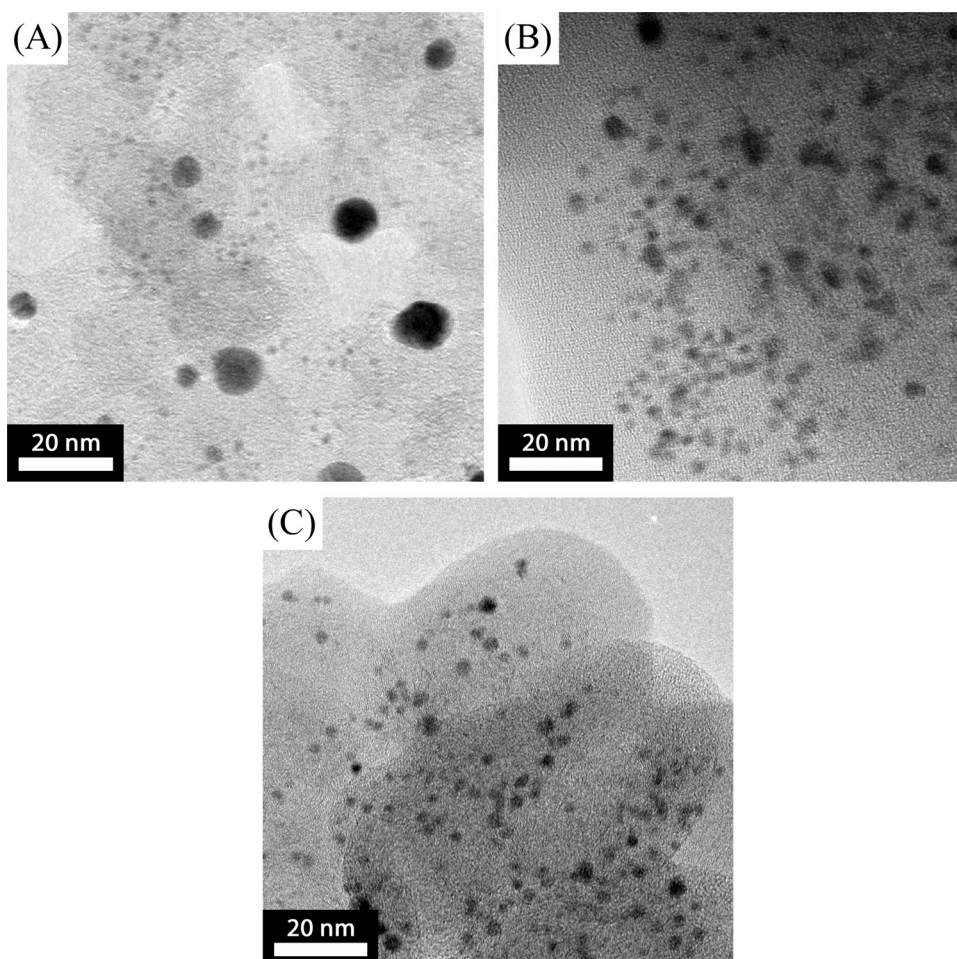

Fig. 1. Representative TEM images of as-prepared Au/C electrocatalysts: (A) 4.5 nm Au, (B) 3.1 nm Au and (C) 2.9 nm Au.