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# Time-Resolved Detection of Surface Oxide Formation at Individual Gold Nanoparticles: Role in Electrocatalysis and New Approach for Sizing by Electrochemical Impacts

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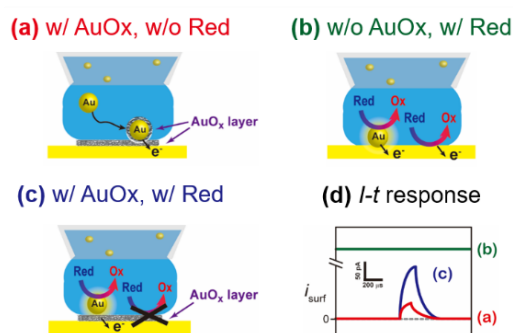
Supporting Information Placeholder

**ABSTRACT:** Nanoparticle (NP) impacts on electrode surfaces has become an important method for analyzing the properties and activity of individual NPs, by either: (i) electrocatalytic reactions; or (ii) volumetric (dissolution) analyses. Using Au NPs as an exemplar system, this contribution shows that it is possible to detect surface oxide formation at individual NPs, which can occur on a rapid timescale (few  $\mu\text{s}$ ). The charge associated with this ‘surface oxidation method’ can be used for sizing (with results that are comparable to TEM) despite charges of only fC being measured. This platform further allows the role of surface oxides in electrocatalysis to be elucidated, with the timescale of oxide formation being controllable (*i.e.*, ‘tunable’) through the applied potential, as illustrated through studies of borohydride and hydrazine electro-oxidation. Finally, all of these studies are carried out on an oxide-covered gold substrate, which can be prepared and regenerated straightforwardly on a gold electrode, through the applied potential.

Single nanoparticle (NP) measurements are a new frontier in electrochemistry.<sup>1</sup> Although experimentally challenging, such measurements bring considerable advantages compared to those on ensembles of NPs on support electrodes, where the response is averaged over many NPs and complicated by the effects of surface coverage, NP distribution and NP-support interactions.<sup>2</sup> Among a limited range of methods, single nanoparticle electrochemical impacts (SNEI) is becoming increasingly popular for detecting and analyzing individual NPs. This typically involves monitoring the current-time ( $I-t$ ) transients associated with the stochastic collision of NPs from a (dilute) colloidal solution with a collector electrode, with the detected current arising from either: (i) a heterogeneous electron-transfer reaction taking place at the NP surface (*e.g.*, electrocatalytic amplification<sup>3-6</sup>); or (ii) the electro-dissolution of the NP itself.<sup>7,8</sup>

In this contribution, we introduce a third approach to investigate the dynamic interaction between metal NPs and a collector electrode, in which the detected current arises from NP surface oxidation, as is shown schematically in Figure 1a for the case of an Au NP. This measurement is much more challenging than the (volumetric) anodic oxidation of metal NPs<sup>7,8</sup>, due to the smaller charges involved and much faster timescale of the process, but opens up new prospects for detecting noble metals and analyzing the formation of surface oxides, which can greatly influence (retard or accelerate) electrocatalysis.<sup>9</sup> Figure 1a highlights a further innovation

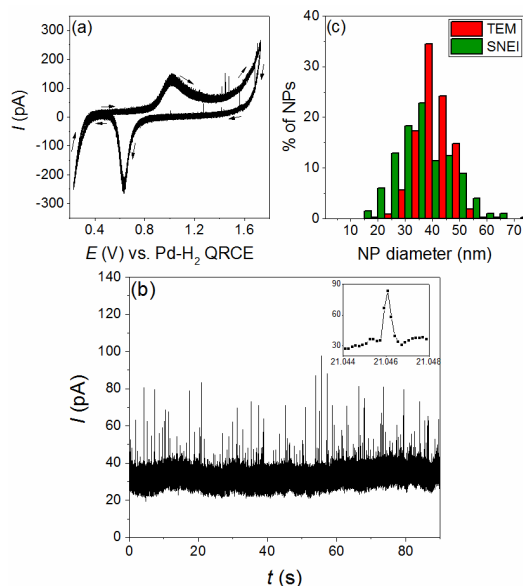
of our work, which is the use of the same material (Au) for the collector electrode as the NPs, with the activity/passivity of the collector electrode controlled through the applied potential. Usually, the potential applied at the Au collector electrode will be sufficiently positive to form gold oxide (*i.e.*,  $\text{AuO}_x$ ), and therefore when Au NPs freely diffusing in solution sporadically make contact with the collector electrode, a small oxidation current ‘blip’ is expected due to the formation of  $\text{AuO}_x$  on the NP surface.<sup>10</sup> A thin layer of  $\text{AuO}_x$  on the Au collector electrode (see Figure 1b) makes it electrochemically inert (*i.e.*, ‘passivated’) towards certain reactions, such as the oxidation of borohydride and hydrazine, considered herein. By maintaining the electrode at a potential where the oxide is stable, individual collisions of Au NPs are detectable through electrocatalytic amplification (see Figure 1c) which competes with NP deactivation through oxide formation. The resulting oxidation  $I-t$  (‘blip’) response thus informs on the electrocatalytic process at a NP surface while undergoing passivation. This will be larger in magnitude than that obtained in the absence of the electroactive species (*e.g.*, see Figure 1d).



**Figure 1.** Schematic of a single NP collision event at an Au collector electrode surface which is: (a) passive (*i.e.*, w/  $\text{AuO}_x$ ), with no redox species present in solution (*i.e.*, w/o Red); (b) active (*i.e.*, w/o  $\text{AuO}_x$ ), with redox species present in solution (*i.e.*, w/ Red); and (c) passive, with redox species present in solution. The  $I-t$  response expected for the NP landing events shown in (a), (b) and (c) are shown in (d) as red, green and blue traces, respectively.

The experimental setup employed in this study is shown schematically in the supporting information (SI), Figure S1a and is based on scanning electrochemical cell microscopy (SECCM)<sup>11</sup>, which has previously been shown to be advantageous in many applications, notably SNEI<sup>12-14</sup>, due to flexibility of electrode size

(determined by the area of meniscus contact) and material, as well as greatly enhanced signal/noise compared to alternative configurations.<sup>2</sup> In this approach, a microdroplet electrochemical cell is formed through contact of the meniscus that protrudes from the end of a tapered micropipet (see SI, Figures S1b and c) with a polycrystalline Au surface. The diameter of the cell ('droplet') is comparable to the diameter of the probe (*i.e.*,  $7 \pm 1 \mu\text{m}$ , see SI, Figure S1d). Note that in this work, we used a single-channel pipet, rather than a dual channel (theta) pipet used previously.<sup>13,14</sup> The citrate capped Au NPs for the landing experiments were synthesized using a literature procedure<sup>15</sup> (representative TEM image shown in SI, Figure S2a) and had an average diameter of  $39 \pm 6 \text{ nm}$  (histogram of size distribution shown in SI, Figure S2b).



**Figure 2.** (a) A CV ( $v = 100 \text{ mV s}^{-1}$ ) obtained in a solution containing 20 mM NaOH and 44 pM Au NPs at an Au collector electrode formed by meniscus contact with a  $7 \pm 1 \mu\text{m}$  diameter micropipet. The arrows indicate the direction of the voltammetric sweep. (b)  $I-t$  trace at 1.6 V (vs. Pd-H<sub>2</sub> QRCE) in a solution containing 20 mM NaOH and 44 pM Au NPs. Inset is a zoomed in view of a ‘typical’ landing event, taking place at 21.046 seconds. (c) Normalized NP diameter distributions from TEM (red bars,  $N = 479$ ) and analysis of the charge passed (green bars,  $N = 202$ ) during landing events under the conditions outlined in (b).

We first consider the detection of Au NPs through the current arising from NP surface oxidation, as shown schematically in Figure 1a. A cyclic voltammogram (CV) at an Au collector electrode in a solution containing 20 mM NaOH and 44 pM Au NPs is shown in Figure 2a. The CV starts a potential of 0.6 V (all potentials are against a Pd-H<sub>2</sub> quasi-reference counter electrode, QRCE), and AuO<sub>x</sub> formation and corresponding stripping (reduction) peaks at the collector electrode can be seen at potentials of 1.1 V and 0.7 V on the forward and reverse sweeps, respectively. Moreover, at potentials beyond the AuO<sub>x</sub> formation peak on the outgoing scan, but prior to the stripping peak on the reverse sweep, a series of transient current spikes (or ‘blips’) ranging in size from 10 to 80 pA are evident. These are attributable to the (surface) oxidation of Au NPs in solution, which sporadically make contact with the collector electrode in the potential region where it is passivated.

In order to investigate the dynamic interaction between Au NPs and the Au collector electrode in further detail, an  $I-t$  trace was recorded at an applied potential of 1.6 V, with typical results shown in Figure 2b. Evidently, a series of short  $I-t$  transients (‘blips’) similar to those seen in the Figure 2a are detected. The experimental landing frequency (*ca.* 1 Hz) is comparable to that predicted<sup>3,14</sup> for the diffusion-limited flux of NPs to the collector electrode surface (*ca.*

0.8 Hz). The inset in Figure 2b is a zoomed in view of a ‘typical’ NP landing event; AuO<sub>x</sub> formation occurs on a very rapid timescale at this potential, with a typical ‘event’ lasting *ca.* 500  $\mu\text{s}$ . Evidently, the detection of the rapid  $I-t$  transients associated with AuO<sub>x</sub> formation requires high time resolution (data acquisition rate = 165  $\mu\text{s}/\text{point}$ , with each point being the average of 33 readings of 5  $\mu\text{s}$  intervals), as well as an excellent signal-to-noise (S/N) ratio (<20 pA peak-to-peak background current). Note that this timescale is convoluted to some extent by the electrometer response and data acquisition rate. We show below that when the AuO<sub>x</sub> formation process is set in competition with electrocatalysis, one can obtain an even better estimate of the AuO<sub>x</sub> formation timescale.

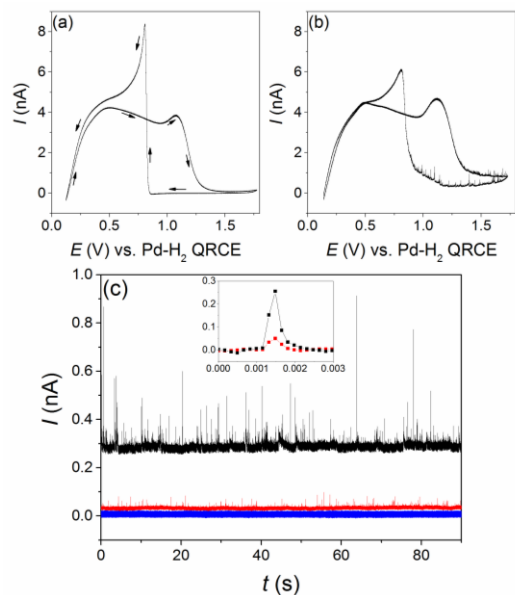
It is reasonable to consider that the charge ( $Q$ ) passed during each landing event (*i.e.*, from integrating the  $I-t$  transients) is proportional to the surface area of the reacting NP (surface oxidation). Calculating the diameter of a NP from  $Q$  requires knowledge of: (i) the oxidation state of the gold in AuO<sub>x</sub>; (ii) surface atom density, which is lattice plane dependent; and (iii) the shape of the NPs. In aqueous alkaline media and at the potential investigated (*i.e.*, 1.6 V vs. Pd-H<sub>2</sub> QRCE), bulk Au is expected to undergo a 2e<sup>-</sup> oxidation to form a monolayer of Au(OH)<sub>2</sub> and/or AuO.<sup>10</sup> By assuming that the Au NPs are spherical and the same oxidation mechanism also applies to the NP surface (*i.e.*,  $n = 2$  and monolayer AuO<sub>x</sub> coverage), and taking the surface atom density of Au in the NPs to be  $10^{15} \text{ atoms cm}^{-2}$  [calculated for the (100) plane of a fcc crystal with a lattice constant of 4.07 Å], a NP size distribution was constructed from  $Q$ , as shown in Figure 2c. The shape of the distribution is in good agreement with the one constructed by TEM image analysis (also shown in Figure 2c), with the main difference being that the histogram constructed by  $Q$  is broader (mean diameter =  $39 \pm 10 \text{ nm}$ ) than from TEM (mean diameter =  $39 \pm 6 \text{ nm}$ ). The smallest NP diameter measurable under the conditions shown in Figure 2 (limited by the S/N) would *ca.* 17 nm. There may be scope for improving this in the future. Overall, the concurrence between the two histograms shown in Figure 2c highlights the capability of this new ‘surface oxidation method’ (see Figure 1a) for NP sizing analysis. This is particularly important because, as mentioned above, a number of noble metals are not easily oxidized but do form oxides and, further, this is a non-destructive analysis method (the surface oxidation could be reversed if needed). In addition, using this method, there may be scope for extracting information on the kinetics of oxide formation at the single NP level in future studies.

The next experimental setup investigated is shown schematically in Figures 1b and c, using borohydride oxidation as the ‘model’ electrocatalytic process (*e.g.*, Red = [BH<sub>4</sub>]). A CV obtained on an Au collector electrode in a 20 mM NaOH solution containing 2.0 mM NaBH<sub>4</sub> is shown in Figure 3a. On gold electrodes, borohydride undergoes the following complicated, 8e<sup>-</sup> oxidation to produce borate (BO<sub>2</sub><sup>-</sup>) and H<sub>2</sub>O in alkaline media<sup>16,17</sup>:



In Figure 3a, on the forward sweep, starting from a potential of 0.13 V, the current rapidly rises to a ‘plateau’ (*ca.* 4 nA), which spans the potential region 0.5 to 1.1 V, before rapidly decreasing to approximately zero, due to surface deactivation (‘passivation’). On the reverse sweep, the Au surface remains inactive until a potential of *ca.* 0.8 V, where the current rapidly rises and peaks at *ca.* 8 nA, before dropping back down to the ‘plateau’ value of 4 nA, and then retracing the voltammetric behavior from the forward sweep. The abrupt deactivation (*ca.* 1.1 V) and activation (*ca.* 0.8 V) of the Au electrode coincide with the formation and stripping of AuO<sub>x</sub>, respectively (see Figure 2a), demonstrating the strong electrode-surface dependence of the [BH<sub>4</sub>]<sup>-</sup> oxidation process. Taking into account that the diffusional flux in SECCM and related droplet-based techniques (*e.g.*, see SI, Figure S1a) is *ca.* 13% of that for the same sized disc electrode<sup>11</sup>, and assuming that the number of electrons transferred is 8 (see Eq. 1) and the diffusion coefficient of [BH<sub>4</sub>]<sup>-</sup>

in alkaline media is  $1.6 \times 10^{-5} \text{ cm}^2 \text{ s}^{-1}$ ,<sup>16</sup> a steady-state limiting current of  $3.5 \pm 0.5 \text{ nA}$  is expected from a droplet diameter of  $7 \pm 1 \mu\text{m}$ , which is in excellent agreement with that observed experimentally in Figure 3a, suggesting that the  $[\text{BH}_4]^-$  oxidation process can attain mass-transport control. It should be noted that the CV obtained at an Au substrate with the microdroplet cell setup qualitatively resembles that obtained at a similarly sized Au ultramicroelectrode (UME, shown in SI, Figure S3), except that the measured current (and hence diffusional flux) at the UME is approximately ten times larger, as expected.<sup>11,14</sup>



**Figure 3.** CVs ( $v = 100 \text{ mV s}^{-1}$ ) obtained from the oxidation of 2.0 mM  $[\text{BH}_4]^-$  (from  $\text{NaBH}_4$ ) in a solution containing 20 mM NaOH and (a) 0 pM or (b) 44 pM Au NPs at an Au collector electrode formed by meniscus contact with a  $7 \pm 1 \mu\text{m}$  diameter micropipet. (c)  $I-t$  curves obtained at a applied potential of 1.6 V (vs.  $\text{Pd-H}_2$  QRCE) in solutions containing 20 mM NaOH together with: 2.0 mM  $[\text{BH}_4]^-$  (blue trace); 44 pM Au NPs (red trace); 2.0 mM  $[\text{BH}_4]^-$  + 44 pM NPs (black trace). Inset is a zoomed in view of ‘typical’ landing events obtained in the presence and absence of  $[\text{BH}_4]^-$ , taking place at 47.318 and 21.046 seconds, respectively.

Shown in Figure 3b is a CV obtained under the conditions outlined above, but with the addition of Au NPs (44 pM). The shape of the CV is very similar to Figure 3a, except for a series of current transients (‘blips’) that are present in the region where the Au collector electrode is passive on both the anodic and cathodic scans (see schematic shown in Figure 1c). The increased size of the current spikes (50 to 600 pA) relative to when no  $[\text{BH}_4]^-$  is present (10 to 80 pA, see Figure 2) indicates that they must arise from both borohydride oxidation and oxide formation, as discussed below.

Shown in Figure 3c are  $I-t$  traces obtained at a collector electrode potential of 1.6 V in the presence or absence of  $[\text{BH}_4]^-$  and Au NPs. In the presence of  $[\text{BH}_4]^-$  and absence of Au NPs (blue trace), a miniscule, constant current of *ca.* 10 pA is observed, indicating that the oxide-covered Au substrate is not particularly active towards borohydride oxidation, consistent with Figure 3a. As discussed above (Figure 2c), in the absence of  $[\text{BH}_4]^-$ , but in the presence of Au NPs (red trace), current ‘blips’ ranging in size from 10 to 80 pA (superimposed on a background current of *ca.* 30 pA) are observed, which arise from the surface oxidation of impacting NPs. In the presence of both  $[\text{BH}_4]^-$  and Au NPs (black trace), much larger current ‘blips’ ranging in size from 25 to 600 pA (superimposed on a background current of *ca.* 300 pA) are observed. Inset is a zoomed in view of a ‘typical’ landing event in the presence or absence of borohydride: the current transient is of a similar duration (*ca.* 500

$\mu\text{s}$ ), because the reaction in both cases is shut off when the NP is surface-oxidized. The charge passed in the presence of  $[\text{BH}_4]^-$  (93 fC) is about 5 times higher than in its absence (18 fC), again, due to both borohydride oxidation and oxide formation. Subtracting the average charge from oxide formation (16 fC) from the total charge passed in this feature gives an estimate of the charge passed due to borohydride oxidation (77 fC), and assuming the full  $8e^-$  process takes place at the NP surface, this corresponds to the oxidation of just *ca.* 100 zmol of  $[\text{BH}_4]^-$  during the event shown in the inset of Figure 3c.

In a number of previous studies<sup>3,17,18</sup>, it has been highlighted that it is often impossible to distinguish whether a current ‘blip’ response arises due to a non-sticking interaction between the NP and collector electrode (*e.g.*, Kang et al.<sup>14</sup>) or due to deactivation of the NP after it ‘sticks’ on the collector electrode surface (*e.g.*, Robinson et al.<sup>19</sup>). In the present study, at the applied potential (1.6 V) it has been confirmed that the NPs deactivate rapidly upon landing (see Figure 2), and given that the NPs and the collector electrode are made from the same material (Au), there is a very high probability that the current ‘blip’ response is due to a ‘sticking interaction’ followed by rapid deactivation. This is consistent with the experimentally measured landing frequency (*vide supra*) and is further confirmed by changing the applied potential. As shown in the SI, Figure S4, at an applied potential of 1.2 V, the current transients decay on a much slower timescale (ms to s) because of the slower rate of surface oxidation of the Au NP. But the longer duration indicates that the NPs must remain in contact with the collector electrode surface. As a consequence, the charge passed during each landing event in the presence of  $[\text{BH}_4]^-$  is much larger at this collector electrode potential (*e.g.*, *ca.* 8 pC in the inset of Figure S4). In effect, the shape and characteristics of the current-time transients (*i.e.*, the timescale of NP deactivation) can be ‘tuned’ by controlling the potential applied at the collector electrode.

A histogram showing the distribution of the peak currents obtained at 1.6 V in the presence of both  $[\text{BH}_4]^-$  and Au NPs is shown in SI, Figure S5. Although a few ‘large’ current transients (*i.e.*, >400 pA) were observed, the majority are smaller than 100 pA (mean peak current is 81 pA). This is much smaller than the diffusion-controlled steady-state current ( $i_{ss} \approx 400 \text{ pA}$ ) predicted for a 39 nm diameter NP on a surface, calculable from<sup>2</sup>:

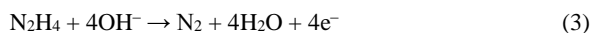
$$i_{ss} = 4\pi(\ln 2)nFDCr_{\text{NP}} \quad (2)$$

where  $n$  is the number of electrons transferred,  $F$  is Faraday’s constant,  $D$  and  $C$  are the diffusion coefficient and bulk concentration of  $[\text{BH}_4]^-$  and  $r_{\text{NP}}$  is the radius of the NP. A steady-state electrocatalytic current would be expected to be established rapidly (governed by the characteristic steady-state diffusion time,  $\approx r_{\text{NP}}^2/D \approx 0.3 \mu\text{s}$ ). The fact that a peak current is observed that is greatly attenuated (about 20% of that expected) means that deactivation ( $\text{AuO}_x$  formation) occurs on a comparable timescale (few  $\mu\text{s}$ ), a small fraction of the electrometer time constant<sup>13</sup>, at 1.6 V.

The few landing events that produced peak currents which are larger than predicted by Eq. 2 are thought to arise from NP aggregates, which form as a result of the addition of  $\text{NaBH}_4/\text{NaOH}$ . NP aggregation is increasingly recognized as important in NP impact studies.<sup>8,19,20</sup> This was confirmed by performing dynamic light scattering (DLS, see the inset of SI, Figure S6), where the average size of the NPs (aggregates) increased continuously with time, after mixing. Furthermore, the influence of aggregation on the SNEI experiments was investigated by performing a measurement 1 hour after solution preparation; as shown in SI, Figure S6, the observed current spikes are, on average, much larger than those seen in Figure 3c, which was recorded in a ‘fresh’ solution.

In a final set of experiments, the setup outlined in Figures 1b and c was used with Red = hydrazine. A CV obtained on an Au substrate in a 20 mM NaOH solution containing 2.0 mM

[N<sub>2</sub>H<sub>5</sub>][HSO<sub>4</sub>] is shown in SI, Figure S7a. Hydrazine undergoes the following 4e<sup>-</sup> oxidation to produce N<sub>2</sub> and H<sub>2</sub>O in alkaline media<sup>21</sup>:



The shape and characteristics of the CV are discussed in detail in the Supporting Information. Shown in SI, Figure S7b is a CV obtained under the same conditions outlined above, except in the presence of 44 pM of Au NPs. Again, the shape of the CV is very similar to that obtained in the absence of Au NPs (see SI, Figure S7a), except a series of current transients ('blips') are observed in the region where the Au collector electrode is not active (*i.e.*, 1.7 to 0.65 V on the reverse sweep only). The inset of SI, Figure S7b is an *I-t* trace obtained at a hold potential of 1.1 V after taking the potential to 1.75 V; *I-t* transients ranging in size from 50 to 300 pA (200 pA expected from Eq. 2), which typically decay on a 10 to 100 ms timescale are observed under these conditions. Again, the observed 'blip' response is attributable to the deactivation of the Au NP by surface oxidation (forming AuO<sub>s</sub>), as discussed above.

In conclusion, the landing of Au NPs on an (oxidized) Au surface have been detected electrochemically with high time resolution, either through the direct oxidation of the NP surface or electrocatalytic amplification, using the oxidation of borohydride and hydrazine as illustrative examples. Au NP surface oxidation goes to completion on a rapid timescale (*ca.* 500 μs), but can be detected with high precision, and the charge associated with this process can be used to estimate the NP surface area, demonstrating the possibility of the 'surface oxidation method' for NP size analysis. With electrocatalytic amplification in this setup, it is possible to assess the impact of surface oxide formation on electrocatalysis, with the timescale of deactivation being controllable through the collector electrode potential. Finally, NP impact studies have tended to use a dissimilar (more inert) collector electrode material compared to the NP, but this study has shown that Au NPs can be detected on an Au electrode, with the surface oxidation state (passivity) carefully tuned via the applied potential.

## ASSOCIATED CONTENT

### Supporting Information

Full experimental details, CVs obtained at UMEs and additional NP landing experiments in the presence of [BH<sub>4</sub>]<sup>-</sup> or hydrazine. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interests.

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# TOC Graphic:

