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COMMUNICATION

## Capping agent promoted oxidation of gold nanoparticles: Cetyl trimethylammonium bromide

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**Capping agents, key for nanoparticle stability, may hugely influence chemical behaviour. We show that differently capped gold nanoparticles, with either citrate or cetyl trimethylammonium bromide (CTAB) capping agents, show qualitatively different electron transfer properties. Specifically through cyclic voltammetry and nanoimpact studies the CTAB promoted dissolution of gold nanoparticles is shown, highlighting the active role which capping agents can play in charge transfer.**

### Introduction

The synthesis of materials on the nanoscale is well-established, having been largely driven by their interesting and potentially advantageous size dependent properties including optical, electronic and (electro)catalytic activities.<sup>1</sup> While such altered properties bring with them much promise for their use in real world applications, it is known that the limited stability of nanoparticles can be problematic, causing the nanoparticles to aggregate to an extent which inhibits their application. One of the major ways this problem is addressed is by the introduction of capping agents to the nanoparticle surface during their synthesis. These capping agents are employed for numerous reasons, such as tailoring the nanoparticle size, modifying their growth on particular crystal facets (as is widely exploited in the growth of nanorods) and reducing the extent of nanoparticle agglomeration through electrostatic and/or steric repulsion.<sup>2</sup> However while the use of such capping agents can increase the stability of the nanoparticles this may lead to changed performance such as lowered catalytic activity.<sup>2</sup> It is therefore critical to consider not only the size, shape and composition of nanomaterials in regards to their applications but the nature of the capping agent must also be

addressed.

In order to probe such behaviour electrochemical investigations have been successfully employed using nanomaterial modified electrodes. This approach has proved to be an extremely effective method to study the behaviour of nanomaterials, with a large number of studies showing that a quantitative understanding of the structure and composition of a range of nanomaterials can readily be attained. In addition electrochemical studies have also been extended to the *single* nanoparticle level. This can be achieved through the Brownian motion driven impacts of individual nanoparticles with an electrode surface, with the nanoparticles then adopting the applied potential and acting as nanoelectrodes.<sup>3-7</sup> Upon impacting the nanoparticles may then be quantitatively dissolved to study their size and composition or investigate their electrocatalytic activity in the absence of any ensemble effects<sup>8</sup> or the loss of nanoparticles from the electrode surface.<sup>3-7,9</sup> This powerful technique has been utilised to determine the composition and reactivity of metallic (e.g. Au, Ag, Pt, Cu, Ni), metal oxide (Fe<sub>3</sub>O<sub>4</sub>) or even organic nanoparticles (such as indigo nanoparticles), demonstrating its ability to study the properties of a wide range of nanomaterials.<sup>3</sup>

In this work we explore and contrast the electrochemical oxidation of gold nanoparticles capped with two commonly employed capping agents, citrate and CTAB. Through the use of cyclic voltammetry and nanoimpact studies the influence of the capping agents on the charge transfer behaviour of the nanoparticles is clearly established, resulting in either the dissolution of the nanoparticles or the formation of a monolayer gold oxide.

### Experimental

All solutions were prepared using Milli-Q water (resistivity of 18.2 MΩ cm at 25 °C) and degassed by bubbling with N<sub>2</sub> prior to performing experiments. Chemicals were used as received from Sigma Aldrich (Potassium bromide and cetyl trimethylammonium bromide) and Fisher Chemicals (HNO<sub>3</sub>).

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CTAB-capped gold nanoparticles (average diameter of  $25.2 \pm 5.5$  nm) and citrate-capped gold nanoparticles (average diameter of  $62.8 \pm 4.4$  nm) were purchased from Nanopartz (Colorado, U.S.A.), sized by Transmission Electron Microscopy (TEM, see below) and used as received.

Electrochemical experiments were performed at  $25 \pm 0.2$  °C using a  $\mu$ Autolab II potentiostat (Metrohm) with a double Faraday cage to minimize electrical noise. A three electrode configuration was used for all electrochemical experiments, with a platinum wire counter electrode and a mercury/mercurous sulphate reference electrode (MSE, saturated  $K_2SO_4$ , measured at +0.399 V vs SCE). This reference electrode was selected in order to avoid any interference of chloride during the experiments, and all potentials presented in this work are quoted versus MSE. Working electrodes for cyclic voltammetry experiments consisted of either a polycrystalline gold electrode (CH Instruments, 2 mm diameter) or Kapton tape masked glassy carbon plates (HTW, 4 mm diameter). Electrodes were cleaned between experiments by polishing on felt pads with decreasing sizes of alumina powder (1  $\mu$ m, 0.3  $\mu$ m and 0.05  $\mu$ m particle sizes) before being thoroughly washed.

For nanoparticle impact experiments carbon fibre microcylinder electrodes were fabricated according to a previously established method.<sup>10</sup> Briefly this involved attaching a carbon fibre (Goodfellow, 7  $\mu$ m diameter) to a wire through the use of silver epoxy (RS Components) and curing at 90 °C for 15 minutes. The carbon fibre modified wires were then immobilised in a micropipette tip using a cyanoacrylate glue (Permabond 102) and allowed to cure overnight. The exposed carbon fibres were then cut to a length of ca. 1 mm.

Nanoparticle size characterisation was performed using TEM with a JEOL JEM-2100 with an accelerating voltage of 200 kV. Sample preparation was performed by drop casting nanoparticle suspensions on holey carbon TEM grids and allowing to air dry.

## Results and Discussion

In order to study the influence of the capping agents on the electrochemical behaviour of the gold nanoparticles, studies were performed using both cyclic voltammetry and nanoimpact experiments, as are discussed in the following sections.

### Cyclic Voltammetry Studies

Cyclic voltammetry was first performed using citrate-capped gold nanoparticle modified glassy carbon electrodes in 0.1 M  $HNO_3$  aqueous solution (Fig. 1a). This system was chosen because in the absence of halide ions gold is known<sup>11</sup> to form a monolayer oxide during the forward scan in the applied potential range of up to +1.1 V vs MSE. This oxide is then reduced in the reverse scan, creating well-defined conditions to systematically investigate the influence of the capping agents. Shown in Fig. 1a is the response of the citrate-capped gold nanoparticles, where a broad oxidative feature (at ca.

0.90 V) can be seen towards the upper potential limit of the scan. This is attributed to both the formation of a monolayer oxide on the drop cast gold nanoparticles as well as the oxidation of the glassy carbon substrate, in agreement with prior work.<sup>12,13</sup> The presence of the gold monolayer oxide can be more clearly identified through the distinct reduction peak on the reverse scan at ca. 0.44 V which is attributed to the quantitative reduction of the monolayer gold oxide formed in the forward scan. To test whether the presence of the citrate capping agent significantly altered the electrochemical behaviour of the gold nanoparticles a gold macro electrode was analysed (Fig. 1b). There the monolayer oxide formation can be observed by the peak at ca. 0.86 V on the forward scan before its subsequent quantitative reduction on the reverse scan at ca. 0.39 V, also in agreement with previous work.<sup>11</sup> These results clearly demonstrate that monolayer oxide formation and reduction dominate the electrochemical response of gold in 0.1 M  $HNO_3$ , as has been well established for a range of acids, and that these processes are comparable in the presence or absence of the citrate capping agent.

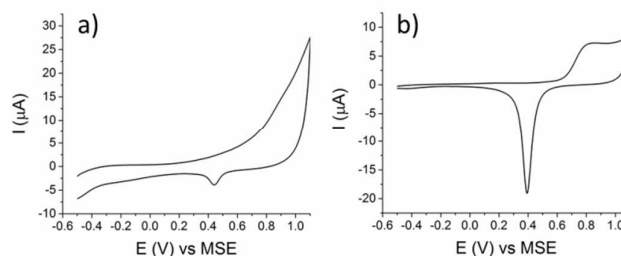
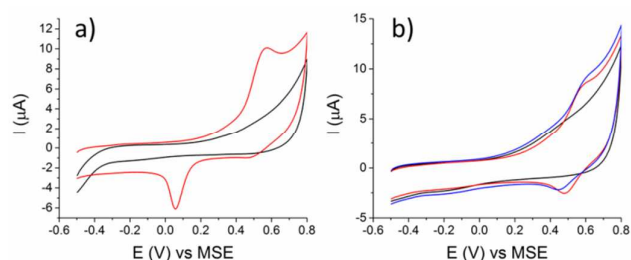


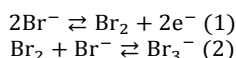
Fig. 1 Cyclic voltammograms of 2  $\mu$ L of citrate-capped gold nanoparticles drop cast on glassy carbon (a) and a gold macro electrode (b) recorded between -0.5 V and 1.1 V at a scan rate of  $50 \text{ mV s}^{-1}$  in 0.1 M  $HNO_3$ .

Cyclic voltammetry was next performed on drop cast CTAB-capped gold nanoparticles, and as can be seen from Fig. 2a (red curve) this resulted in an oxidative peak (0.57 V) in the forward scan and a reductive peak (0.06 V) in the reverse scan. These processes occur at significantly lower potentials than the monolayer oxide formation and reduction peaks which were observed on the gold macro electrode (0.84 V and 0.39 V, respectively). Citrate-capped gold nanoparticles were also examined in this potential region (Fig. 2a, black curve), however no clear redox processes were observed as the upper potential limit of 0.8 V was not high enough to cause detectable oxidation of the citrate-capped gold nanoparticles. It should be noted that these differences are not attributed to nanoparticle size related effects, in light of similar voltammetry recorded at 20 nm diameter citrate-capped gold nanoparticles.<sup>13</sup> Comparison of the citrate- and CTAB-capped gold nanoparticle responses immediately highlights that the CTAB capping agent not only acts to stabilise gold nanoparticles from aggregation in solution but that it can also significantly alter the electrochemical reactivity of the nanoparticles.

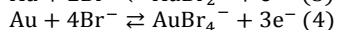


**Fig. 2a)** Cyclic voltammograms of 2  $\mu\text{L}$  of citrate-capped gold nanoparticles (black) or 8  $\mu\text{L}$  of CTAB-capped gold nanoparticles (red) drop cast on glassy carbon electrodes recorded at a scan rate of  $50 \text{ mV s}^{-1}$  in  $0.1 \text{ M HNO}_3$ . **b)** Cyclic voltammograms of bare glassy carbon electrodes in  $0.1 \text{ M HNO}_3$  in the absence (black) or presence of  $0.1 \text{ mM CTAB}$  (red) or  $0.1 \text{ mM KBr}$  (blue) recorded at a scan rate of  $50 \text{ mV s}^{-1}$ .

To understand the nature of these processes voltammetry was then performed using an unmodified glassy carbon electrode in  $0.1 \text{ M HNO}_3$  (Fig. 2b, black curve). Here the oxidation of the glassy carbon surface can be observed, and upon the introduction of  $0.1 \text{ mM CTAB}$  to the solution (red curve) an oxidation peak at ca.  $0.57 \text{ V}$  and reduction peak at ca.  $0.48 \text{ V}$  are visible, demonstrating that CTAB is electrochemically active in this region. Similar experiments where the CTAB was replaced with  $0.1 \text{ mM KBr}$  (blue curve) display a strong similarity to the CTAB response with an oxidative peak at ca.  $0.59 \text{ V}$  and a reductive peak at ca.  $0.45 \text{ V}$ , showing that the electrochemical response of the CTAB is due to the oxidation and reduction of bromide to bromine (Equation 1) which may be followed by the reaction of bromine with bromide to form tribromide (Equation 2).<sup>14,15</sup>

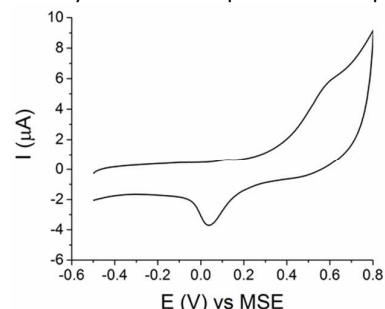


By contrasting the voltammograms in Fig. 2b with the CTAB-capped gold nanoparticles in Fig. 2a (red curve) it can be seen that the oxidation potential of both the CTAB-capped gold nanoparticles and solution phase CTAB occur at similar potentials, although the reduction peak at ca.  $0.06 \text{ V}$  for the former sample does not correlate with the reduction of bromine (ca.  $0.48 \text{ V}$ ). This is instead attributed to the reduction of gold species which formed through dissolution during the forward scan,<sup>16-18</sup> indicating that the oxidative signal is due to both the oxidation of bromide as well as the dissolution of gold through either a one electron (Equation 3) or a three electron oxidation (Equation 4).<sup>19,20</sup>



The voltammetry of the citrate-capped gold nanoparticles was then investigated in the presence of  $0.1 \text{ M HNO}_3$  with  $0.1 \text{ mM CTAB}$  to determine whether this could induce a similar response to CTAB-capped gold nanoparticles in  $0.1 \text{ M HNO}_3$ . Shown in Fig. 3 the citrate-capped gold nanoparticles in the presence of  $0.1 \text{ mM CTAB}$  indeed showed a similar voltammetric profile to the CTAB-capped gold nanoparticles (Fig. 2a, red curve), with an oxidation peak at ca.  $0.58 \text{ V}$  and a reductive peak at ca.  $0.04 \text{ V}$ . This provides further evidence that while CTAB is utilised to increase the stability of the nanoparticles in solution such capping agents, usually introduced to stabilise nanomaterials, can in fact *promote* the reactivity of the nanoparticles in electrochemical systems. This

is demonstrated in the current case through the electrochemical dissolution of the gold nanoparticles, due to the introduction of the CTAB or its dissociation to form free bromide in solution. Hence the influence of capping agents must be carefully considered when studying the electrochemical behaviour of nanoparticles, as has been highlighted recently in the case of platinum nanoparticles.<sup>21</sup>

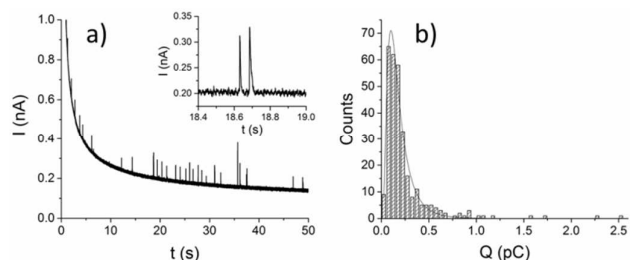


**Fig. 3** Cyclic voltammograms of 2  $\mu\text{L}$  of citrate capped gold nanoparticles in  $0.1 \text{ M HNO}_3$  in the presence of  $0.1 \text{ mM CTAB}$ , recorded at a scan rate of  $50 \text{ mV s}^{-1}$ .

### Nanoimpact Experiments

Owing to the close overlap of the  $\text{Br}^-$  oxidation and gold dissolution responses these processes were further studied using nanoimpact experiments, where the electrochemical behaviour of single nanoparticles can be analysed. This technique involves the application of a fixed potential to an electrode in a solution containing nanoparticles, where the Brownian motion driven impact of nanoparticles with the electrode surface allows the nanoparticles to be addressed on an *individual* basis. By altering the applied potential to the electrode surface the nanoparticles then behave as nanoelectrodes upon impact with the electrode, providing a powerful tool to study the electrochemical behaviour of individual nanoparticles.

In the present work nanoimpact experiments were performed using carbon fibre microcylinder electrodes, owing to their ability to measure low concentrations of nanoparticles (even at femtomolar concentrations).<sup>9,10</sup> Impacts were achieved using a solution of  $1 \text{ pM CTAB}$ -capped gold nanoparticles in  $0.1 \text{ M HNO}_3$ , with an applied potential of  $0.7 \text{ V}$  selected based on the cyclic voltammogram shown in Fig. 2a (red curve). As can be seen from Fig. 4a this resulted in the presence of numerous oxidative spikes in the chronoamperograms, which are clearly distinguishable from the background electrical noise.



**Fig. 4a)** Chronoamperogram recorded at  $0.7 \text{ V vs MSE}$  at a microcylinder electrode in  $0.1 \text{ M HNO}_3$  with  $1 \text{ pM CTAB}$ -capped gold nanoparticles. The distribution of impact charges is shown in **b)** along with the log-normal fit of the data.

In order to ensure that these spikes were indeed related to the oxidation of the gold nanoparticles a number of rigorous



control experiments were performed. Firstly the electrochemical behaviour of the carbon fibre electrodes was tested in a solution of 0.1 M HNO<sub>3</sub> at 0.7 V (Fig. S1) to ensure that the carbon fibre electrodes do not give rise to any spike-like features. Secondly, the potential dependency of the nanoparticle impacts was established by switching the potential from 0.7 V to 0.4 V, where no impacts are expected at the latter potential as demonstrated by the voltammogram in Fig. 2a. This was confirmed through the results shown in Figs. S2 and S3, where no impacts were observed at a potential of 0.4 V (Fig. S2) however impacts were again seen upon returning the applied potential to 0.7 V (Fig. S3). Finally, in light of recent work which demonstrated the electrochemical detection of CTAB micelles through nanoimpacts under high CTAB concentrations,<sup>22</sup> experiments were performed at 0.7 V in a solution of 0.1 M HNO<sub>3</sub> with 0.15 mM CTAB to ensure that the oxidative spikes were not the result of the impact of CTAB micelles. As can be seen from Fig. S4 this did not result in the presence of spikes in the chronoamperograms, but instead the oxidation of bromide from the CTAB was observed as an increased background current compared with 0.1 M HNO<sub>3</sub> alone (Fig. S1). These results conclusively verify that the spikes seen in the presence of the gold nanoparticles were not due to the oxidative impact of CTAB micelles but the electrochemical dissolution of the gold nanoparticles.

Having established the nature of the spikes which were observed in the presence of the gold nanoparticles, the charges were then measured by integrating the 300 recorded impacts. Shown in Fig. 4b these charges followed a log-normal distribution with a mean charge of ca. 0.15 pC. In order to determine the average particle size, TEM analysis was performed on the CTAB-capped gold nanoparticles revealing an average diameter of 25.2 ± 5.5 nm. From this value the number of moles of gold per nanoparticle was calculated (ca. 8.2 × 10<sup>-19</sup> moles), and by comparing this value with the experimentally obtained oxidative charge the average number of electrons transferred during the oxidation of each gold atom was found to be 1.9. This indicates that the process does not occur as a quantitative 3 electron process by the direct oxidation of Au to AuBr<sub>4</sub><sup>-</sup> (Equation 4), as has been assumed in a number of analytical studies, but a significant proportion of AuBr<sub>2</sub><sup>-</sup> is also generated (Equation 3). This result is in agreement with work by Ivanova and Zamborini<sup>19</sup> who reported a value of 1.5 electrons for the oxidation of gold in the presence of bromide. Note, however, that the shape and size distribution of gold nanoparticles are more tightly controlled in the current study compared with the electrodeposited gold nanoparticles used in the earlier study. In addition the use of nanoimpact experiments in this work provides the means to address individual nanoparticles rather than giving an ensemble average.

## Conclusions

The electrochemical behaviour of gold nanoparticles was found to be greatly influenced by the nature of the capping agent. Studies using cyclic voltammetry in 0.1 M HNO<sub>3</sub> show that citrate-capped gold nanoparticles behave very differently from CTAB-capped gold nanoparticles, with the latter nanoparticles oxidising at significantly lower potentials. This altered behaviour is attributed to the introduction of Br<sup>-</sup> to the

system through the CTAB capping agent, resulting in both the oxidative dissolution of gold as well as the oxidation of Br<sup>-</sup> to Br<sub>2</sub> at suitable potentials. Nanoimpact studies differentiated between these processes, as the recorded spikes were solely due to the oxidative dissolution of impacting gold nanoparticles. In this manner the dissolution of gold in the presence of Br<sup>-</sup> was quantitatively analysed, demonstrating that the oxidation of each gold atom produced an average of 1.9 electrons. This finding reveals that the dissolution of the gold nanoparticles in the presence of bromide proceeds through the formation of both Au(I) and Au(III) species.

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## Notes and references

1. M.-C. Daniel and D. Astruc, *Chem. Rev.*, 2004, **104**, 293-346.
2. Z. Niu and Y. Li, *Chem. Mater.*, 2014, **26**, 72-83.
3. W. Cheng and R. G. Compton, *TRAC, Trends Anal. Chem.*, 2014, **58**, 79-89.
4. A. J. Bard, H. Zhou and S. J. Kwon, *Isr. J. Chem.*, 2010, **50**, 267-276.
5. M. Pumera, *ACS Nano*, 2014, **8**, 7555-7558.
6. N. V. Rees, *Electrochem. Commun.*, 2014, **43**, 83-86.
7. M. Kang, D. Perry, Y.-R. Kim, A. W. Colburn, R. A. Lazenby and P. R. Unwin, *J. Am. Chem. Soc.*, 2015, DOI: 10.1021/jacs.5b05856.
8. K. Tschulik, C. Batchelor-McAuley, H.-S. Toh, E. J. E. Stuart and R. G. Compton, *Phys. Chem. Chem. Phys.*, 2014, **16**, 616-623.
9. B. J. Plowman, K. Tschulik, E. Walport, N. P. Young and R. G. Compton, *Nanoscale*, 2015, **7**, 12361-12364.
10. J. Ellison, C. Batchelor-McAuley, K. Tschulik and R. G. Compton, *Sens. Actuators, B*, 2014, **200**, 47-52.
11. S. G. D. Shackelford, C. Boxall, S. N. Port and R. J. Taylor, *J. Electroanal. Chem.*, 2002, **538-539**, 109-119.
12. L. E. Barrosse-Antle, L. Xiao, G. G. Wildgoose, R. Baron, C. J. Salter, A. Crossley and R. G. Compton, *New J. Chem.*, 2007, **31**, 2071-2075.
13. Y.-G. Zhou, N. V. Rees, J. Pillay, R. Tshikhudo, S. Vilakazi and R. G. Compton, *Chem. Commun.*, 2012, **48**, 224-226.
14. P. K. Adanuvor, R. E. White and S. E. Lorimer, *J. Electrochem. Soc.*, 1987, **134**, 1450-1454.
15. G. D. Simpson and R. E. White, *J. Electrochem. Soc.*, 1990, **137**, 1843-1846.
16. A. Pearson, A. P. O'Mullane, V. Bansal and S. K. Bhargava, *Chem. Commun.*, 2010, **46**, 731-733.
17. S. Meltzer and D. Mandler, *J. Electrochem. Soc.*, 1995, **142**, L82-L84.
18. B. J. Plowman, N. Thompson and A. P. O'Mullane, *Gold Bull.*, 2014, **47**, 177-183.
19. O. S. Ivanova and F. P. Zamborini, *Anal. Chem.*, 2010, **82**, 5844-5850.
20. J. Zheng, W. Huang, S. Chen, Z. Niu and Z. Li, *Electrochem. Commun.*, 2006, **8**, 600-604.
21. J. E. Newton, J. A. Preece, N. V. Rees and S. L. Horswell, *Phys. Chem. Chem. Phys.*, 2014, **16**, 11435-11446.
22. H. S. Toh and R. G. Compton, *Chem. Sci.*, 2015, **6**, 5053-5058.