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Tannic Acid Capped Gold Nanoparticles: Capping Agent Chemistry Controls the Redox Activity

Alex L. Suherman,^a Giorgia Zampardi,^a Hatem M.A. Amin,^a Neil P. Young^b and Richard G. Compton^aReceived 00th Mmm 20xx,
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We report the key role of the capping agent in the detection of metal cations using tannic acid (TA) capped gold nanoparticles at both ensembles (using cyclic voltammetry) and with individual particles (using oxidative and reductive nanoimpacts). The results show that the capping agent complexes with Zn^{2+} and Hg^{2+} in a reversible and Langmuirian manner in both cases. The sensitivity of detection is determined by the amount of capping agent present on the nanoparticles with similar values seen for both oxidation and reduction reactions. The optimisation of the capping agent loading is therefore key to metal ion detection.

Introduction

Understanding the role of the capping agent is important for the development of the controlled synthesis of nanoparticles¹, the prevention of nanoparticle aggregation/agglomeration², the attenuation of nanoparticle toxicity³, the control of nanoparticle reactivity⁴ and for understanding electron-transfer dynamics^{5,6}. In addition, capped nanoparticles such as gold nanoparticle (AuNPs) are widely used notably for colorimetric analysis⁷, electrocatalysis⁸ and electroanalysis⁹. In this paper, we show how the *quantity* of capping agent can control electrochemical responses.

The interaction between the capping agent of nanoparticles and metal cations has been reported to influence the extent of agglomeration of nanoparticles.¹⁰ The latter was found to have a correlation with the metal-capping agent complex formation constant. For example, in the presence of lead(II) cations, silver nanoparticles reversibly form agglomerates and this is induced by the complexation between Pb^{2+} and citrate groups of the capping agent. The capping agent can also tune the electron transfer kinetics to/from the nanoparticle.^{11,12} For example, whilst citrate capped silver nanoparticles are completely oxidised at low potentials, DNA capped particles require higher potentials for complete oxidation and which is enough to oxidise the quinine and adenine base pairs of DNA. This emphasizes the role of DNA capping agent as a tunnelling barrier to insulate the particle core, and thus selectively control of the oxidation process can be realised

by adjusting the applied potential. An electron transfer-gated mechanism has been also observed for poly(ethylene glycol) capping agents, where a dynamic equilibrium between a wrapped and unwrapped silver nanoparticle exists.¹³ Meanwhile, the reactivity of nanoparticles has been studied using cetyl trimethylammonium bromide (CTAB) capping agent.¹⁴ The CTAB shifted the nanoparticle oxidation to significantly lower potentials, resulting in the more facile oxidative dissolution of gold.

Macromolecular capping agents such as tannic acid (TA) have been exploited for the electrochemical detection of specific metal cations via ensembles of the gold nanoparticles.^{15,16} However, the electrochemical analysis of the TA capping agent studied with an ensemble of AuNPs@TA (for example using stripping voltammetry) does not reflect necessarily its behaviour at the individual nanoparticle level. In particular, analysis of the nanoparticles using stripping voltammetry is unreliable because capping agent effects in drop casting may lead to particle aggregation and partial oxidation.^{17,18}

Recent advances in the “nanoimpacts” technique have demonstrated the possibility of electrochemistry at the single particle level^{19–23}. This technique is performed by suspending nanoparticles in solution, so that individual nanoparticle can stochastically collide with an electrode surface due to their Brownian motion. Faradaic current-time transients (“spikes”) in the background reveal the collision events. Usually, the spike is produced from two possible sources: (1) an electrochemical reaction catalysed (“mediated”) on the surface of the collided nanoparticles (“indirect impacts”) and (2) the oxidation or reduction of the single nanoparticle itself when it hits the electrode surface (“direct impacts”).^{23–25} This work will in contrast focus on the electrochemistry of the capping agent on the nanoparticle surface using both oxidative and reductive nanoimpacts to understand the role of a TA capping agent (see Scheme 1) on gold particles for the detection of Zn^{2+} and Hg^{2+} and to generate mechanistic and kinetic insights.

^a Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University, South Parks Road, Oxford, OX1 3QZ, UK.
E-mail: richard.compton@chem.ox.ac.uk

Fax: +44 (0)1865 275410

Tel: +44 (0)1865 275957

^b Department of Materials, Oxford University, Parks Road, OX1 3PH, UK.

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Scheme 1. The TA capping agent controls the redox activity of the gold nanoparticle

Experimental

Chemicals and Reagents

The tannic acid-capped gold nanoparticles (AuNPs@TA, 2.2×10^{10} particles mL^{-1}) colloid, with a hydrodynamic diameter of 68.4 nm as indicated by the manufacturer, were used as received (NanoComposix Inc., San Diego, US). The main ingredients of the supplied suspension are Au (0.005 % mass), tannic acid (<0.001 % mass) and water (>99 % mass). The manufacturer declares²⁶ that “no residual reactants” are present in the final formulation. Zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ $\geq 98\%$, Sigma-Aldrich, Gillingham, UK) and mercury(II) nitrate ($\text{Hg}(\text{NO}_3)_2$ 0.05 M, Sigma-Aldrich, Steinheim, Germany) were used as Zn^{2+} and Hg^{2+} sources, respectively; and were prepared in 0.1 M KCl + 0.1 M HCl solutions^{15,16}. All solutions were prepared using nanopure water with a resistivity of not less than 18.2 M Ω cm at 298K (Millipore, US) and degassed thoroughly with high purity nitrogen flow (BOC Gases plc, UK) before use.

Electrochemical Procedure

Electrochemical experiments were performed in a thermostatted (25 ± 1 °C) Faraday cage using a μ Autolab III potentiostat (Metrohm-Autolab BV, The Netherlands). The 3.0 mm diameter glassy carbon electrode (GCE, CH Instruments, Austin, US) and 7.0 μm diameter carbon microdisc (ALS, Japan) were used as working electrodes for cyclic voltammetry (CV) and nanoimpacts experiments, respectively. A saturated calomel electrode (SCE) (BASi, Japan) and a 0.5 mm diameter platinum wire (Goodfellow Cambridge Ltd., UK) were used as reference and counter electrodes, respectively. Prior to the experiment, both the GCE and the carbon microdisc electrode were polished using alumina slurries of decreasing particle sizes of 1.0, 0.3 and 0.05 μm (Buehler, IL, UK) on soft lapping pads and rinsed with nanopure water in between. To ensure the reproducibility of all measured data, both electrodes were regularly re-polished.²⁷

For CV analysis of Zn^{2+} , ca. 2.0×10^9 particles of the AuNPs@TA suspension were drop-casted on the GCE surface and left under nitrogen atmosphere to dry fully. This resulted in an average one-monolayer surface coverage of AuNPs@TA-GCE (see [SI.1 Calculation Detail](#)). However, the possibility of particles agglomeration/aggregation is recognised in the drop casting method and can drive the incomplete stripping oxidation of the nanoparticles.^{18,28,29} CV were recorded by sweeping the potential

from 0.0 V to 0.7 V and reversed back to 0.0 V vs SCE, at a scan rate of 0.1 V s^{-1} . CV analysis of Hg^{2+} has been reported previously.¹⁶

For nanoimpacts experiments, the chronoamperometry was recorded at a carbon microdisc electrode with the same reference and counter electrodes as above; but using a home-built low noise potentiostat with a post-acquisition Bessel filtering of 100 Hz and PyFemto software (version 0.6).³⁰ This potentiostat accurately conserves the overall amount of charge transferred due to a particle impact process despite possible alteration in the spike shape.^{15,31} Note that all solutions were degassed with nitrogen thoroughly to remove dissolved electroactive oxygen. A 10 pM of AuNPs@TA suspension (ca. 8.8×10^9 particles) and various concentrations of either Zn^{2+} (10 to 300 mM) or Hg^{2+} (1 to 100 μM) were added into the solution containing 10 mM KCl + 10 mM HCl. Chronoamperograms were recorded for 25 s at different oxidizing or reducing potentials. For Zn^{2+} analysis, potentials in the range from 0.4 to 0.7 V and -0.2 to -0.5 V were applied for oxidative and reductive nanoimpacts, respectively. For Hg^{2+} analysis, chronoamperograms were recorded at potentials between 0.6 to 0.9 V and -0.2 to -0.6 V for oxidative and reductive nanoimpacts, respectively. The magnitude of the spike threshold is taken as either three or five times the estimate of the standard deviation of the background noise current.³² The spikes were analysed using “SignalCounter”, which was developed by Dr D. Omanović (Centre for Marine and Environmental Research Zagreb, Croatia).³³

Characterization of AuNPs@TA

Transmission electron microscopy (TEM) imaging of the AuNPs@TA was carried out using a JEOL JEM-3000F instrument with an accelerating voltage of 300 kV. The samples were prepared by drop-casting ca. 2.0×10^9 particles of the AuNPs@TA onto holey carbon grids (Agar Scientific Ltd., UK) and allowing them to dry completely under a nitrogen atmosphere. Subsequent image extraction and analysis were performed using ImageJ software (National Institute of Health, US).

Dynamic light scattering (DLS) analysis was performed to measure the hydrodynamic diameter of the AuNPs@TA. DLS was carried out using Malvern Zetasizer Nano ZS instrument with an irradiation wavelength of 633 nm He-Ne laser. Each sample was diluted with nanopure water and filtered using a sterile Whatman 0.2 μm filter to remove any contaminants before being placed in a disposable solvent-resistant micro-cuvette (path length of 10 mm). Three sets of 12 light scattering measurements were taken and averaged to give three size distributions for the AuNPs@TA. Zetasizer software from Malvern (Malvern Panalytical Ltd., Malvern, UK) was used to analyse the data.

Nanoparticle Tracking Analysis (NTA) was performed with a NanoSight LM10 (NanoSight, Amesbury, UK), equipped with a sample chamber and a 642 nm laser. The samples were injected into the sample chamber with sterile syringes (B&D Discardit II, US) and the absence of air bubbles ensured. Three runs of 60 s each on three different portions of the samples were measured with an automatic setting of 30 frames s^{-1} .

Figure 1. (a) TEM micrograph showing the AuNPs core capped with TA layers. Statistical distributions of (b) diameter size of AuNP core and (c) layer thickness of TA, as extracted from TEM micrographs of 60 particles.

Scanning electron microscopy (SEM) and zeta potential analyses of the AuNPs@TA have been reported previously.^{15,16} Meanwhile, a Shimadzu UV-1800 with 20 μL High Precision Quartz Cells (Hellma Analytics, Germany) was used to measure the stability of the 10 pM of AuNPs@TA in various concentrations of supporting electrolyte. Each solution was outgassed prior to the measurement and followed by performing baseline correction. UV-vis spectra were recorded from 650 to 400 nm of 1 min interval for 15 min.

Results and discussion

We first report the physical characterisation of the AuNPs@TA using TEM, DLS, NTA and UV-vis spectroscopy analyses. Next, the electrochemical analysis of AuNPs@TA was conducted at the ensemble (using CV) and single particle (using nanoimpacts) levels. Subsequently, both oxidative and reductive nanoimpacts experiments were performed in the absence and presence of Zn^{2+} or Hg^{2+} on single particles of AuNPs@TA. Comparisons are used to infer the mechanisms underlying the redox responses observed and the key role of the capping agent identified and defined.

Characterization of AuNPs@TA

Size characterisation of the AuNPs core and thickness of the TA capping agent were carried out using TEM. As shown in Figure 1, the nanoparticle population exhibits qualitative homogeneity in their morphology, namely roughly spheroidal particles. The average diameter size of AuNPs core and thickness of TA capping layers are 62.2 ± 1.4 nm and 8.3 ± 0.5 nm, respectively. DLS and NTA analyses were undertaken to measure the average hydrodynamic diameter (overall sizes) of the AuNPs@TA. The results give an average diameter of 68.1 ± 0.7 nm (based on the mode value) and 68.7 ± 0.4 nm for NTA and DLS analysis, respectively (Figure SI.1). These values are consistent with the data supplied by the manufacturer of the particle²⁶ and with our previous reports.^{15,16}

The stability of the AuNPs@TA in various concentrations of electrolyte were assessed by UV-Vis spectroscopy, in the range of 10 to 100 mM of KCl + HCl solutions. Each electrolyte was outgassed thoroughly with nitrogen before 10 pM of AuNPs@TA (ca. 8.8×10^9 particles) was added. Figure SI.2 depicts the most stable condition of AuNPs@TA in 10 mM KCl + 10 mM HCl solutions with only a ca. 2% decrease in maximum absorbance during 15 min of observation, with the wavelength of 535 nm. The lowest stability was found in 100 mM KCl + 100 mM HCl solutions, with ca. 53% decrease in maximum absorbance. Given the use of 10 mM KCl + 10 mM HCl as supporting electrolyte and the bubbling of solutions with nitrogen between experiments, it is reasonable to conclude that the AuNPs@TA suspensions are stable over the time period (~15 min) of the subsequent particle impacts experiments (see below).

Figure 2. CV analysis of the ensemble of AuNPs@TA (oxidation of TA capping agent to TA-quinone, Scheme 1)

Electrochemical Analysis of AuNPs@TA

Having physically characterized the AuNPs@TA, electrochemical characterization of the ensemble of AuNPs@TA were investigated first using CV. This was achieved by drop casting ca. 2.0×10^9 particles of AuNPs@TA suspension onto a GCE surface, leading to an approximately on average a one-monolayer surface coverage of AuNPs@TA-GCE (SI.1 Calculation Detail). The modified electrode was then immersed in a solution of 0.1 M KCl + 0.1 M HCl and CVs were recorded by sweeping the potential from 0.0 V to 0.7 V and reversed back to 0.0 V vs SCE at a scan rate of 0.1 V s^{-1} .

As shown in Figure 2 (solid black line), a single broad oxidative peak ("peak 1") was observed at potential of ca. 0.31 V vs SCE. This peak is consistent with our previous reports on the oxidation of TA to TA-quinone (see Scheme 1).¹⁵ Also consistent with our previous works^{15,16}, the peak currents of the "peak 1" increased linearly with scan rate, ranging from 0.01 to 0.1 V s^{-1} . The result confirms that the oxidation of the TA capping layers is, as expected, a surface-controlled process (oxidation of adsorbed, non-diffusing material). Furthermore, the peak potentials of the "peak 1" were essentially scan rate independent hinting at an electrochemically reversible process. In our previous work¹⁵, we noted that the peak potential and peak current of the "peak-1" decreased with increasing pH solutions, suggesting the loss of protons on oxidation of the TA capping agent. However, analysis of the ensemble of AuNPs@TA via drop casting method is recognised to effect experimental results by causing aggregation/agglomeration of the capping agent.^{17,28} Therefore, to get an accurate understanding of the role the TA capping agent plays in the electron transfer process, the nanoimpacts technique was next performed.

Single particles of AuNPs@TA were characterised via oxidative nanoimpacts with the aim of calculating the number of electroactive quinone/hydroquinone species in the capping layer involved in the reaction at single AuNPs@TA level. To assess this, a carbon microdisc electrode was immersed in 10 mM KCl + 10 mM HCl solutions (hereafter referred to as the "blank solution") containing 10 pM (ca. 8.8×10^9 particles) of AuNPs@TA. Chronoamperograms were recorded at applied oxidising potential ranging from 0.3 V to 0.7 V vs SCE. In the absence of AuNPs@TA (control experiment), featureless continuous time-current transients were observed at all potentials studied (Figure SI.3). Subsequently, by introducing the AuNPs@TA, the oxidative spikes were observed at applied potential ≥ 0.5 V vs SCE (Figure 3). The lower oxidising potential (0.3 and 0.4 V) gave spike features too

Figure 3. Representative chronoamperogram of carbon microdisc electrode immersed in a blank solution containing ca. 10 pM (ca. 8.8×10^9 particles) AuNPs@TA at potential of 0.6 V vs SCE (inset image depicts the spike shape)

small to detect, suggesting insufficient potential to oxidise the TA capping layers at the individual AuNPs@TA level.

The average spikes charge, current, duration and frequency, resulting from the TA oxidation, were found to be ca. 0.32 ± 0.1 pC, 18.4 ± 3.4 pA, 23.3 ± 4.5 ms, 0.3 ± 0.1 spike s⁻¹, respectively. These values are roughly constant at potentials of ≥ 0.5 V vs SCE (Figure 3). The experimental number of TA molecules incorporated on a single AuNPs core is ca. 1.0×10^5 molecules, calculated by applying the Faraday's first law and considering a maximum of potentially 20 electron transfer from the TA molecular structure¹⁵ (SI.1 Calculation Detail). This result is in good agreement with the apparent number of the TA molecules of ca. 1.2×10^5 molecules as calculated by dividing the volume of AuNP core with an estimated volume of a single TA (8.6×10^{-28} m³) reported by Madhan *et al.*³⁴ (SI.1 Calculation Detail).

Subsequently, reductive nanoimpacts experiments of AuNPs@TA were undertaken by immersing a carbon microdisc electrode in either blank solution (control experiments) or blank solution containing 10 pM (ca. 8.8×10^9 particles) of AuNPs@TA. Chronoamperograms were recorded at applied reducing potential ranging from -0.1 V to -0.5 V vs SCE in each case. As shown in Figure SI.4, both in the absence and in the presence of AuNPs@TA no reductive spike features were observed at all studied potentials. The result suggests that the TA capping agent, incorporated on an individual AuNPs core, is not reduced under these potentials and thus is electrochemically inactive. This is consistent with previously reported data.^{15,16}

The following section considers the role of the TA capping agent in the presence of metal cations. The analysis was again carried out by exposing AuNPs@TA, either as ensembles (using CV) or as single particles (using nanoimpacts), into aqueous solution containing Zn²⁺ or Hg²⁺ ions.

Electrochemical Analysis of AuNPs@TA with Metal Cations

Ensembles of AuNPs@TA in the presence of Zn²⁺ were analysed using CV. A one-monolayer surface coverage of AuNPs@TA-GCE

was immersed in a blank solution containing 1 mM Zn²⁺ and CV were recorded by sweeping the potential from 0.0 V to 0.7 V and reversed back to 0.0 V vs SCE at a scan rate of 0.1 V s⁻¹. As shown in Figure 4 (solid black line), two oxidative peaks were observed at peak potential of 0.31 V ("peak 1") and 0.48 V vs SCE ("peak 2"). The "peak 1" was the result of the oxidation of TA to TA-quinone (see above), whilst "peak 2" is attributed to the oxidation of TA capping agent complexed with Zn²⁺. This leads to the "swelling" of the TA capping layers during oxidation, followed by greater accessibility of the complexing sites to uptake Zn²⁺ and results in "peak-2".^{15,16} CV analysis of the Hg²⁺ has been reported previously, with the "peak 2" was observed at a more positive potential (0.58 V vs SCE).¹⁶ These results suggest that TA capping agent uptakes metal cations.

Next, the effect of scan rate was studied to identify whether the oxidation of the Zn/TA complexes in the ensemble of AuNPs@TA is surface-controlled or diffusion-controlled process. To assess this, the AuNPs@TA-GCE was exposed to a solution containing 1 mM Zn²⁺. Then CVs were recorded at various scan rates between 0.01 and 0.1 V s⁻¹. Note that each experiment was performed using freshly modified electrode and new outgassed analyte solutions.

Figure 4. CV analysis of the ensemble of AuNPs@TA in the presence of Zn²⁺

The peak current value of the “peak 2”, baseline corrected by applying a polynomial fit (typically of order-4), increased linearly ($R^2 = 0.995$) with scan rate (Figure SI.5). The result suggests that the oxidation of AuNPs@TA complexed Zn^{2+} is a surface-controlled process; a similar process as seen with Hg^{2+} as has been reported previously.¹⁶ Moreover, the peak potentials of the “peak 2” were scan rate independent again suggesting an electrochemically reversible process, where the shift in peak potential between “peak 1” and “peak 2” reflects the strength of the binding of Zn^{2+} and TA. Following this, the AuNPs@TA-GCE was immersed in a blank solution containing various Zn^{2+} concentrations ranging from 1 to 120 mM, with an applied scan rate of 0.1 V s^{-1} . Equilibration of the AuNPs@TA with the solution containing the ions, or not, was realised within a matter of minutes.^{15,16} The peak current of “Peak 2” increased with the Zn^{2+} concentration and saturated for concentration above 75 mM (Figure SI.6). This result indicates the limitation of the TA capping agent to uptake Zn^{2+} at concentration beyond 75 mM. In addition, CV analysis of the ensembles AuNPs@TA in the presence of metal cations with different pre-equilibrium times has been reported previously.^{15,16} For example in case of Hg^{2+} , the peak current of “peak 2” increased during a pre-equilibrium time of 10 min. This result suggests that the swelling of TA layer reached its maximum at 10 min when the electrode surface becomes saturated with Hg^{2+} .

Reductive CV scans were studied to identify whether the TA capping agent may mediate the underpotential deposition of zinc on the gold core surfaces within the AuNPs@TA ensemble. Underpotential deposition (UPD) is the deposition of a monolayer or sub-monolayer of metal onto different metal surface at potentials more positive than the Nernst potential for bulk deposition of this metal.^{35,36} A one-monolayer surface coverage of AuNPs@TA-GCE was immersed in a blank solution containing 0.2 mM Zn^{2+} . Subsequently, the reductive CV scan was recorded by sweeping the potential from 0.0 V to -1.2 V and reversed back to 0.0 V vs SCE at a scan rate of 0.02 V s^{-1} . The UPD peak was observed at potential of -0.8 V vs SCE followed by a sharp increase in the cathodic current from potential of ca. -1.0 V to -1.2 V vs SCE (bulk deposition of zinc) (Figure SI.7). The sharp UPD peak shape indicates the reaction is probably not controlled by mass transport to the ensembles of AuNPs@TA surface but suggests that under sufficient reducing potential, the zinc ions can complex with the TA layers and on reduction zinc metal is deposited on the gold core surface. Integrating the UPD peak results in a charge of ca. $17.2 \mu\text{C}$, with an apparent surface coverage of the zinc deposition is ca. $2.2 \times 10^{14} \text{ atoms cm}^{-2}$ (SI.1 Calculation Detail). No UPD signal was seen in the absence of AuNPs@TA.

Having characterised the ensemble of AuNPs@TA in the presence of metal cations using CV, the next section will identify the role of the TA capping agent at single AuNPs@TA in the presence of either Zn^{2+} or Hg^{2+} . The analysis consists of both oxidative and reductive nanoimpacts at various potentials and for different metal cation concentrations.

Oxidative Nanoimpacts Analysis

Initially, control experiments were performed in the absence of the AuNPs@TA. A carbon microdisc electrode was immersed in an outgassed blank solution containing various concentrations of

Figure 5. Representative chronoamperograms of oxidative nanoimpacts using ca. 10 pM (8.8×10^9 particles) AuNPs@TA in the presence of (a) 100 mM Zn^{2+} and (b) $10 \mu\text{M Hg}^{2+}$ at potential of 0.6 V and 0.7 V , respectively.

metal cation, either 10 to 300 mM Zn^{2+} or 1 to $100 \mu\text{M Hg}^{2+}$. The microdisc electrode was held at the potential of 0.4 , 0.5 , 0.6 and 0.7 V vs SCE for Zn^{2+} or 0.6 , 0.7 , 0.8 and 0.9 V vs SCE for Hg^{2+} . No spike features were detected at any studied potential for these control experiments. Following this, ca. 10 pM (8.8×10^9 particles) of AuNPs@TA was introduced into the outgassed blank solution containing of either 100 mM Zn^{2+} or $10 \mu\text{M Hg}^{2+}$, and the potential was applied as with the control experiments.

As shown representatively in Figure 5, clear and sharp oxidative spikes were observed for both of the metal cations studied. The results suggest that the oxidative spikes result from oxidation of the TA capping agent upon collision of the nanoparticles with the electrode surface (see Scheme 1). In this process, hydroquinone groups are oxidised to the quinone form.¹⁵ As shown in Figure 6, the spike magnitude (charge, current, duration and frequency) were found to be similar but a little larger in the presence of metal cations as compared to the case of the uncomplexed AuNPs@TA. The small increase in charge and current may reflect swelling of TA layer promoting the oxidation of more quinone groups (see above) whilst the duration and frequency may hint at electrostatic factors being drops by the complexation.

To study the potential dependency, the average charge of $2,114$ spikes at four different potentials (0.4 to 0.7 V vs SCE) were calculated and plotted as a function of different Zn^{2+} and Hg^{2+} concentrations. As shown in Figure SI.8, the average charge values were found to be roughly constant at all potentials studied. Note that potentials lower than 0.4 V gave features too small to detect. The charge values increased up to 30 mM Zn^{2+} , saturating at higher concentrations (Figure SI.8). In comparison, 1 to $100 \mu\text{M}$ of Hg^{2+} were assessed in the same manner as with the Zn^{2+} , but at applied potentials of 0.6 V to 0.9 V vs SCE. The average charge values were found to be roughly constant at all studied potentials (0.5 , 0.6 and 0.7 V for Zn^{2+} and 0.6 , 0.7 , 0.8 and 0.9 V for Hg^{2+}). The charge values in the presence of Hg^{2+} increased up to $25 \mu\text{M Hg}^{2+}$, again saturating at higher concentrations (Figure 6a, red).

Following this, the oxidative spikes charge, current, duration and frequency for both Zn^{2+} and Hg^{2+} were plotted and compared together (Figure 6). Notably, these characteristics were shown to have an approximately similar qualitative behaviour in both cases but, quantitatively, responding differently to the metal cation concentration. For example, a similar behaviour of impact duration of 20 – 35 ms and frequency of ca. 0.3 – $0.4 \text{ spikes s}^{-1}$ were observed at concentration region of $\leq 30 \text{ mM Zn}^{2+}$ and $\leq 25 \mu\text{M Hg}^{2+}$, above which the value tend to plateau at higher concentrations but, significantly, with similar values for each case.

Figure 6. Overlaid plots of the average oxidative spikes charge (a), current (b), duration (c) and frequency (d) in the presence of various Zn^{2+} (black) and Hg^{2+} (red) concentrations.

These results suggest that TA controls the oxidation process prior to the complexation with metal cations and undergo oxidation in a similar manner for both metals.

Reductive Nanoimpacts Analysis

For comparison, reductive nanoimpacts were also studied. The reductive nanoimpacts experiments were performed by immersing a microdisc electrode in an outgassed solution containing the same concentrations of either Zn^{2+} or Hg^{2+} as in the oxidative nanoimpacts experiments. The potential was applied at -0.2 V to -0.5 V vs SCE for Zn^{2+} and -0.2 to -0.6 V vs SCE for Hg^{2+} . Initially, the control experiments were performed in the absence of the AuNPs@TA at different metal cation concentrations and at various potentials. No reductive spikes were detected for all control experiments. Next, by introducing a ca. 10 pM (8.8×10^9 particles) AuNPs@TA the sharp reductive spikes were detected for both cations (Figure 7). The spikes result from the collision events of the single AuNPs@TA with the electrode surface, which subsequent deposition of Zn^0 or Hg^0 on the electrode surface during the impact residence time.

Figure 7. Representative chronoamperograms of reductive particle impacts using ca. 10 pM (8.8×10^9 particles) AuNPs@TA in the presence of (a) 100 mM Zn^{2+} and (b) 10 μM Hg^{2+} at potential of -0.2 V and -0.4 V, respectively.

Figure 8. Overlaid plots of the average reductive spikes charge (a), current (b), duration (c) and frequency (d) in the presence of various Zn^{2+} (black) and Hg^{2+} (red) concentrations.

In the presence of Zn^{2+} , the average reductive charge values were found to be roughly constant at all studied potentials (Figure SI.9) and, significantly, were similar to the values seen for the oxidative nanoimpacts. Analogous behaviour was found in the presence of Hg^{2+} with similar values of the reductive spikes current, duration and frequency at oxidative and reductive nanoimpacts. As shown in Figure 8, the average spikes charge, current, duration and frequency were compared together as function of different Zn^{2+} and Hg^{2+} concentrations. Importantly, these characteristics show roughly similar values as seen for the oxidative nanoimpacts (see Figure 6), but different onsets of with respect to the metal cation concentrations. These results suggest that TA controls both oxidation and reduction activity of the nanoparticle (Scheme 1).

Mechanistic Insights

The charge vs Zn^{2+} or Hg^{2+} concentration data for AuNPs@TA was analysed using the Langmuir adsorption model. The Langmuir isotherm can be expressed as follows: $\theta = KC / (1 + KC)$, where θ is the fractional coverage that is directly related to the charge, K is the equilibrium constant of adsorption and C is the metal cation concentrations. The data was analysed by selecting the charge vs concentration data before saturation (≤ 30 mM for Zn^{2+} and ≤ 25 μM for Hg^{2+}). As shown in Figure 9a, the reciprocal charge was plotted

Figure 9. Langmuir plots of a) Zn^{2+} and b) Hg^{2+} on single particles AuNPs@TA for oxidative and reductive nanoimpacts. Langmuir model applies with cation concentration before saturation (≤ 30 mM of Zn^{2+} , ≤ 25 μM of Hg^{2+}).

against reciprocal of Zn^{2+} concentrations giving straight lines with $R^2 = 0.988$ and $R^2 = 0.995$ for oxidative and reductive nanoimpacts, respectively. The linearity indicates that the complexation of Zn^{2+} onto TA capping agent at individual AuNPs@TA level is consistent with the Langmuir model. The adsorption constant (K), as estimated from the reciprocal of the slope from oxidative and reductive nanoimpacts, were seen to have a similar value of ca. 0.1 mM^{-1} for both the oxidative and reductive nanoimpacts of Zn complexed particles. Interestingly, the complexation of Zn^{2+} seen at the ensembles of AuNPs@TA was also Langmuirian at concentration region of $\leq 75 \text{ mM}$ Zn^{2+} (before saturation) with an adsorption constant of $K = 0.12 \pm 0.003 \text{ mM}^{-1}$ (Figure S1.11). The similar value of the adsorption constant of Zn at both ensemble and individual AuNPs@TA levels confirms the suggested complexation mechanism, which is Langmuirian.

For comparison, the Langmuir adsorption model was also applied to Hg^{2+} for oxidative and reductive nanoimpacts (Figure 9b). At the concentration region of $\leq 25 \text{ }\mu\text{M}$, the linearity was found with $R^2 = 0.995$ ($K = 0.13 \pm 0.003 \text{ }\mu\text{M}^{-1}$) and $R^2 = 0.986$ ($K = 0.12 \pm 0.002 \text{ }\mu\text{M}^{-1}$) for oxidative and reductive nanoimpacts, respectively. The adsorption constant in the presence of Zn^{2+} or Hg^{2+} , for both oxidative and reductive nanoimpacts, was found to be roughly similar values although the order of magnitude of the adsorption concentration differed by three orders of magnitude between the two metals. This result suggests that the complexation of both metal cations undergo similar manner, in which TA capping agent controls the redox activity.

Conclusions

The TA capping agent markedly controls the redox activity of the nanoparticle, prior to and after the complexation with either Zn^{2+} or Hg^{2+} . The maximum uptake of these metal cations reflects the amount of capping agent that can undergo redox activity. Analogous redox behaviour of the metal cation complex TA-coated particles was observed for both Zn^{2+} and Hg^{2+} : the processes are Langmuirian, surface-controlled and an electrochemically reversible process, giving similar values for oxidative and reductive signals for both metals. However, the adsorption equilibration constant for Zn^{2+} is three orders of magnitude higher than that of Hg^{2+} . It is evidenced that the quantity and limit of detection (LOD) of the metals is controlled by the amount of TA used to cap the nanoparticles.

Conflicts of interest

There are no conflicts to declare.

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SUPPORTING INFORMATION

Tannic Acid Capped Gold Nanoparticles: Capping Agent Chemistry Controls the Redox Activity

Alex L. Suherman¹, Giorgia Zampardi¹, Hatem M. A. Amin¹, Neil P. Young², Richard G. Compton^{1,*}

¹Department of Chemistry, Physical and Theoretical Chemistry Laboratory, Oxford University,
South Parks Road, Oxford OX1 3QZ, UK.

²Department of Materials, Oxford University, Parks Road, OX1 3PH, UK.

1. Calculation Details

Concentration of AuNPs@TA suspension = 2.2×10^{10} particles ml^{-1}

Surface area of glassy carbon electrode (πr_e^2), $r_e 1.48 \pm 0.02$ mm, = ca. 6.9×10^{-6} m^2

Radius of core AuNP, r_p , is 31.1 nm

1.1. Ensembles Particle Level

(a) **Number of AuNPs@TA particles** onto GCE surface for one-monolayer surface coverage, N , considering closest packing of equal sphere of 91%, calculated as follow:

$$N = 0.91 * \frac{\text{Surface area of GCE}}{\text{Surface area of AuNPs@TA}} = 0.91 \frac{\pi r_e^2}{\pi r_p^2} = \text{ca. } 2.0 \times 10^9 \text{ particles}$$

(b) **Total surface area of AuNPs@TA** drop-cast onto GCE surface, A , calculated as follow:

$$A = N * (4\pi r_p^2) = 2.0 \times 10^9 \text{ particles} * (1.2 \times 10^{-14} \text{ m}^2) = 2.4 \times 10^{-5} \text{ m}^2$$

1.2. Individual Particles Level (Nanoimpacts)

From the oxidative nanoimpacts experiment with the absence of the metal cations (oxidation of TA capping agent), the average spikes charge, Q , was found to be ca. 0.3 pC.

The number of moles, n , of TA involved in the reaction is calculated using Faraday's first law:

$$n = \frac{Q}{zF}$$

where, z is the number of electron transfer during oxidation of TA (assuming fully oxidised, $z = 20$) and F is the Faraday's constant ($96485.33 \text{ C mol}^{-1}$). The number of moles TA was found to be ca. 1.6×10^{-19} or equal to **ca. 1.0×10^5 molecules**.

Meanwhile, the apparent number of TA molecules incorporated in a single AuNP core was calculated by dividing volume of AuNP core with known volume of a single TA molecule ($8.6 \times 10^{-28} \text{ m}^3$)²³

$$N_{\text{TA}} = \frac{1.07 \times 10^{-22} \text{ m}^3}{8.6 \times 10^{-28} \text{ m}^3} = \text{ca. } 1.2 \times 10^5 \text{ molecules.}$$

1.3. Underpotential Deposition (UPD) of Zinc onto Ensembles of AuNPs@TA

- From CV experiments, reductive charge of the Zn (UPD), Q , is ca. $17.2 \mu\text{C}$.
- Surface coverage of 0.2 mM Zn^{2+} UPD ($z = 2$, F is Faraday constant $96485.33 \text{ C mol}^{-1}$ and $A = 2.4 \times 10^{-5} \text{ m}^2$ is total surface area of one-monolayer of AuNPs@TA drop casted onto GCE surface) calculated as follow:

$$\begin{aligned} &= \frac{Q}{zFA} \\ &= \frac{17.2 \times 10^{-6} \text{ C}}{(2) \cdot (96485.33 \text{ C mol}^{-1}) \cdot (0.24 \text{ cm}^2)} \\ &= \text{ca. } 3.7 \times 10^{-10} \text{ mol cm}^{-2} \\ &= \text{ca. } 2.2 \times 10^{14} \text{ atoms cm}^{-2} \end{aligned}$$

2. Supporting Figures

2.1. Characterisation of AuNPs@TA

Figure SI.1. Characterization of the AuNPs@TA using (a) NTA and (b) DLS analysis

Figure SI.2. UV-vis analysis of AuNPs@TA. (a) UV-vis spectra of ca. 10 pM AuNPs@TA in a solution of 10 mM KCl + 10 mM HCl, (b) Plot of peak absorbance of AuNPs@TA in various electrolyte concentrations during 15 mins.

2.2. Electrochemical Analysis of AuNPs@TA

Figure SI.3. Oxidative particle impacts analysis. Representative chronoamperograms of microdisc electrode immersed in solution containing of 10 mM KCl + 10 mM HCl at potential of 0.4, 0.5, 0.6, 0.7 V vs SCE.

Figure SI.4. Reductive particle impacts analysis. Representative chronoamperograms of microdisc electrode immersed in solution containing of (a) blank and (b) AuNPs@TA + blank at potential of -0.3, -0.4, -0.5 V vs SCE.

2.3. Electrochemical Analysis of Ensembles of AuNPs@TA with Metal Cations

Figure SI.5 (a) Cyclic voltammograms of one-monolayer surface coverage of AuNPs@TA-GCE at various scan rates, (b) Linearity of peak current of the "peak 2" at various scan rates shown in (a).

Figure SI.6. (a) Cyclic voltammograms of one-monolayer surface coverage of AuNPs@TA-GCE at various concentrations of Zn²⁺. (b) Plot of peak current of the "peak 2" at various concentrations of Zn²⁺

Figure SI.7. Underpotential deposition of Zn²⁺ at the ensembles of AuNPs@TA, at a scan rate of 0.02 V s⁻¹

2.4. Particle Impacts Analysis of Individual AuNPs@TA with Metal Cations

Figure SI.8. Linear relationship between average spikes: (a) charge, (b) current, (c) duration and (d) frequency with different potentials at various Zn^{2+} concentrations, resulting from oxidative and reductive particle impacts

Figure SI.9. Reductive particle impacts. Linear relationship between average spikes: (a) charge, (b) current, (c) duration and (d) frequency with potentials at various Zn^{2+} concentrations (potential of -0.2, -0.3 and -0.5 V).

Figure SI.10. Linear relationship between average spikes: (a) charge, (b) current, (c) duration, (d) frequency at various Hg^{2+} concentrations, resulting from oxidative and reductive particle impacts (potential of -0.2 to -0.6 V)

Figure SI.11. Langmuir plot of Zn^{2+} on ensembles AuNPs@TA (before saturation) with $K = \text{ca. } 0.11 \text{ mM}^{-1}$