Anodic Stripping Voltammetry of Silver Nanoparticles: Aggregation Leads to Incomplete Stripping

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The influence of nanoparticle aggregation on anodic stripping voltammetry is reported. Dopamine-capped silver nanoparticles were chosen as a model system, and melamine was used to induce aggregation in the nanoparticles. Through the anodic stripping of the silver nanoparticles that were aggregated to different extents, it was found that the peak area of the oxidative signal corresponding to the stripping of silver to silver(I) ions decreases with increasing aggregation. Aggregation causes incomplete stripping of the silver nanoparticles. Two possible mechanisms of 'partial oxidation' and 'inactivation' of the nanoparticles are proposed to account for this finding. Aggregation effects must be considered when anodic stripping voltammetry is used for nanoparticle detection and quantification. Hence, drop casting, which is known to lead to aggregation, is not encouraged for preparing electrodes for analytical purposes.
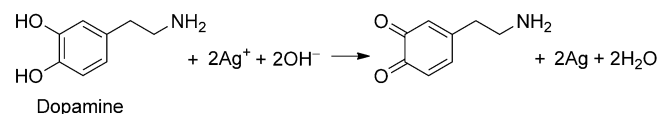
Anodic stripping voltammetry is a sensitive electrochemical method widely applied to the detection of metals and organic materials.[1] Its sensitivity lies in the pre-concentration step, which amplifies the signal generated from a small quantity of analyte.[1] Recently, the method has been used to detect and quantify redox-active nanoparticles.[2] Examples include nanoparticles made of silver, fullerene, oil blue dye, molybdenum, and indigo.[2a–f, i–m, r–t] One of the most common pre-concentration strategies is the use of drop casting. It involves depositing a nanoparticle suspension onto the electrode and evaporating the solvent to leave a layer of nanoparticles on the electrode surface before voltammetric analysis.[3] A study of anodic stripping voltammetry of silver nanoparticles, accompanied by scanning electron microscopy (SEM), has revealed that during the solvent evaporation procedure, the drop casting technique can lead to extensive nanoparticle aggregation.[4] This can cause a significant difference in size between the nanoparticles

on the modified electrode and the nanoparticles in suspension.[4]

According to the IUPAC Compendium of Chemical Terminology (the Gold Book), aggregation and agglomeration are referred to as the irreversible or reversible sticking together of particles respectively.[5] The irreversible aggregation of nanoparticles has effects on many physical and chemical properties.[6] For instance, the thermal conductivity of nanoparticles can change due to the presence of a highly conductive percolation path with increasing aggregation.[6a] The percolation path is a result of increasing contact between the particles, creating pockets to trap heat. Another example is the changing dissolution rate of silver nanoparticles. As it is strongly linked to the surface area to volume ratio, the rate of silver ion release varies inversely with the degree of aggregation.[6d, 7]

A change in chemical properties between aggregated and nonaggregated nanoparticles was reported by Jassby et al., in that the photocatalytic generation of hydroxyl radical from hydroxide ion decreased with increasing aggregation of the nanoparticles.[6b] This was explained by two factors. First, by increasing the size of the nanoparticles, the surface area available for chemical reaction decreases, thus decreasing the nanoparticle reactivity.[6b] Second, the increasing contact between the nanoparticles allowed quenching of electron holes between the neighbouring particles, decreasing the efficiency of photocatalytic generation of hydroxyl radicals.[6b] These examples show that nanoparticle aggregation has a strong influence over diverse chemical and physical properties. Nonetheless, the effect of aggregation on analytical methods is still not fully understood. Therefore, the present work aims to determine any influence of aggregation on the important electrochemical technique of anodic stripping voltammetry.

Silver nanoparticles were chosen as a model system. Dopamine-capped silver nanoparticles can be easily synthesised by mixing sodium hydroxide, dopamine, and silver nitrate, with dopamine acting both as a reducing agent and as a capping agent.[8] Scheme 1 depicts dopamine reducing silver(I) ions, Ag^+, to silver(0), Ag, in alkaline conditions.[9] In turn, dopamine is converted into its quinone form and attaches onto the silver nanoparticle as the capping agent serving to stabilise the nanoparticles.[8]
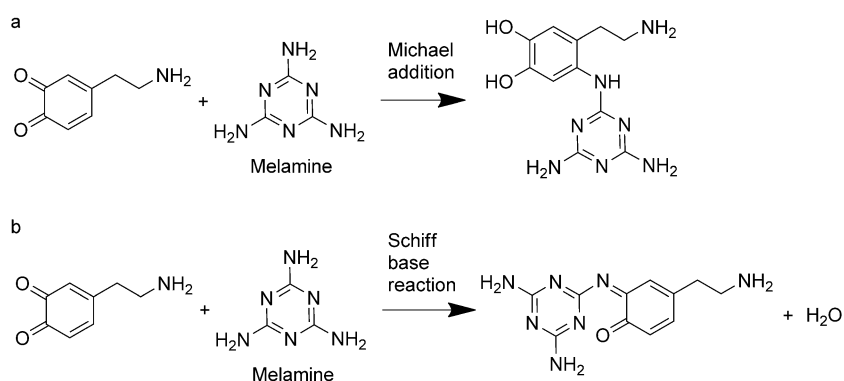
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Scheme 1. Reduction of silver(I) ions to silver by dopamine.

Scheme 2. a) Possible Michael addition reaction between oxidised dopamine and melamine. b) Possible Schiff base reaction between oxidised dopamine and melamine.
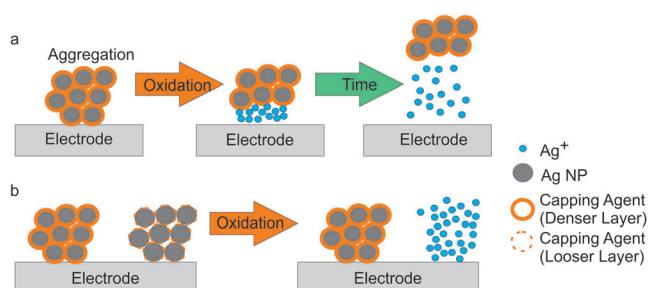
The peak area under the signal is generally used as an indication of the quantity of analyte present on the electrode.[2a–d] By taking the area underneath the signal, an average of 6.72×10^{-6} C is recorded. This corresponds to a silver surface coverage of 9.9×10^{-10} moles cm^{-2}. Assuming 100% silver oxidation on the electrode, dopamine has converted 15% of the silver ions into recovered silver nanoparticles. Thus, the average peak area obtained can be used as a refer-

To induce aggregation, melamine can be added during the synthesis of dopamine-capped silver nanoparticles.[10] In alkaline conditions, reports have suggested that the melamine might covalently bond to dopamine stabilised silver nanoparticles, via two possible reaction routes summarised in Scheme 2 a,b.[8, 10]

The first route is a Michael addition where melamine reacts with the aromatic nucleus of the quinone to form a C–N bond.[10] The second mechanism is Schiff-base addition that links the quinone moiety with melamine through a C=N bond.[10a] The three amine groups of melamine can individually react with three quinone groups, helping to cross link nanoparticles and induce aggregation. In the study reported here, a working electrode is modified with nanoparticles aggregated to different degrees controlled by the amount of melamine added; then it is stripped oxidatively. The changes in voltammetric responses with regard to the varying degrees of aggregated nanoparticles reflect the significant effect of aggregation on anodic stripping voltammetry.
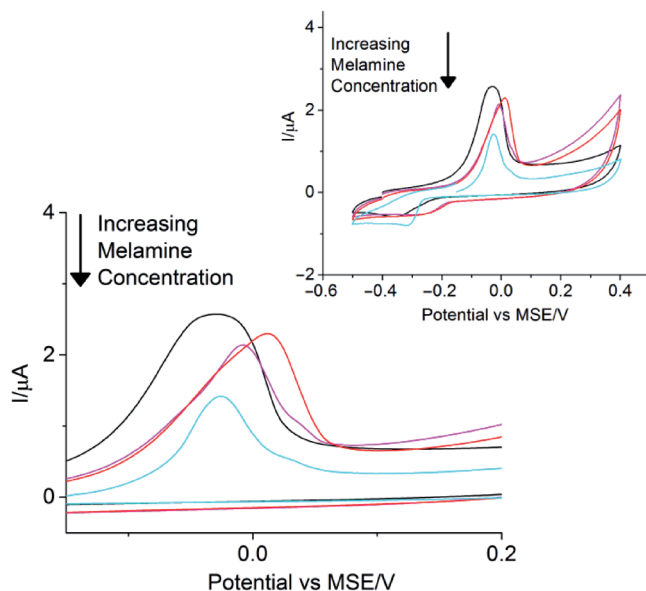
Anodic stripping voltammetry was performed on variously synthesised silver nanoparticles to investigate the effect of aggregation. Initially, the dopamine-capped silver nanoparticles were synthesised in the absence of melamine to determine their electrochemical behaviour. Next, different concentrations of melamine were added to nanoparticle synthesis to induce varying degrees of aggregation. The voltammograms of the dopamine-capped silver nanoparticles aggregated to different extents are summarised below. It was found that aggregation causes the incomplete stripping of nanoparticles, and Scheme 3 depicts possible mechanistic scenarios that may result in incomplete stripping.

Initially, dopamine-capped silver nanoparticles were synthesised in the absence of melamine to determine their electrochemical behaviour.[8] The silver nanoparticle suspension was drop cast on a glassy carbon electrode, and the modified electrode was oxidatively stripped in aqueous sodium nitrate (0.10 M) via anodic stripping voltammetry. An oxidation signal (~0.0 V vs. standard mercury/mercurous sulfate electrode [MSE]) corresponding to the oxidation of silver to silver(I) ions is observed in the voltammogram (black line in Figure 1).[11]


Scheme 3. Two possible explanations for the incomplete stripping of aggregated silver nanoparticles. a) 'Partial oxidation' where silver nanoparticles are lost from the surface after partial oxidation. b) 'Inactivation' where a more compact layer of capping agent around the silver nanoparticles hinders complete silver oxidation relative to a less compact layer.

Figure 1. The oxidation of dopamine-capped silver nanoparticles, synthesised in the presence of different concentrations of melamine, on a glassy carbon electrode in sodium nitrate (0.1 M) at a scan rate of 50 mVs^{-1}. Black: No melamine; Pink: 15 μM; Red: 50 μM; Cyan: 1000 μM. Inset: full voltammograms.

ence value to compare with the aggregated nanoparticles in the later paragraphs.

To investigate the effects of aggregation on anodic stripping voltammetry, the dopamine-capped silver nanoparticles were then synthesised in the presence of different amounts of melamine. By studying the voltammetric response generated by the nanoparticles, a clearer understanding of the effects of aggregation on anodic stripping voltammetry was gained. The suspensions synthesised with different melamine concentrations were separately drop cast on electrodes and oxidatively stripped. Three repeats were performed for each experiment, and the average reproducibility was about 17%. Figure 1 depicts typical voltammograms recorded for the silver nanoparticles synthesised with the melamine concentrations of 0 μM, 15 μM, 50 μM, and 1000 μM in sodium nitrate (0.10 M). An oxidation signal (peak potential ~0.0 V vs. MSE) was observed for the silver nanoparticles aggregated to different extents. Hence, similar to the results reported above, the signal corresponds to the oxidation of silver to silver(I) ions.[11] The peak area under the oxidative signal was measured, and it was observed that the peak area has a negative correlation with the concentration of melamine present during nanoparticle synthesis. A wide range of melamine concentrations ranging from 0–1000 μM was tested. From Figure 2, it was found that the oxi-
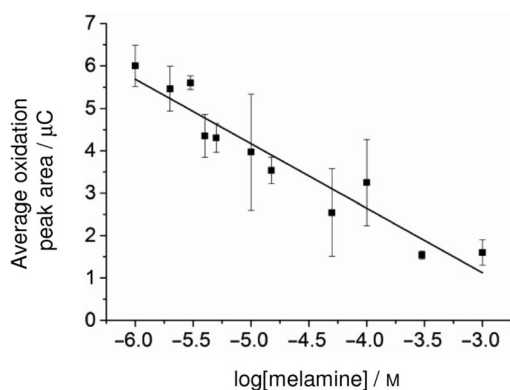
Figure 2. Plot of average oxidation peak area (of dopamine-capped silver nanoparticles) against log[melamine]. Each data point consists of a minimum of three repeats.

dation peak area is systematically lower for the nanoparticles synthesised in the presence of melamine compared to the control experiments (see above). The decrease in oxidation peak area approximately scales in a linear way with log[melamine], with an empirical equation of $Q(C) = -3.44 \times 10^{-6}$ (log[melamine/M]) $- 1.52 \times 10^{-6}$. It is thought that with the increasing amount of melamine present, more cross links between the dopamine-capped silver nanoparticles are formed, resulting in a greater extent of aggregation among the nanoparticles.[9–10]

As increasing aggregation leads to a decrease in stripping peak area, incomplete stripping of the nanoparticles has likely occurred, and it may be accounted for by two possible mechanisms. First, Scheme 3a shows 'partial oxidation' of an aggregated particle; only the nanoparticles inside the aggregated particle that are in contact with the electrode are oxidised into

silver(I) ions. Hence, the rest of the aggregated particle lose electrical contact to the electrode as the silver(I) ions dissolve, leaving them largely intact. Thus, the remainder of the nanoparticles inside the aggregated particle are not oxidised. Therefore, with increasing aggregation, the proportion of nanoparticles in contact with the electrode surface decreases, resulting in 'partial oxidation' of silver nanoparticles. Another possible mechanistic scenario is depicted in Scheme 3b, namely the 'inactivation' of aggregated particles. Here, there are two (or more) species of silver nanoparticles. The first species of nanoparticles is completely surrounded with a denser layer of capping agent consisting of dopamine and melamine. The denser layer might hinder the oxidation process of silver to silver(I) ions, hence 'inactivating' the silver nanoparticles. The second species is again of aggregated particles but with a looser layer of capping agent. When an oxidative potential is applied, only the second species will be oxidised into silver(I) ions. As more melamine is present during the synthesis process, the proportion of aggregates with the denser capping agent layer increases, which leads to an increase in 'inactivation' of the silver nanoparticles. Therefore, considering Scheme 3, silver nanoparticle aggregation may result in incomplete stripping through 'inactivation' or/and 'partial oxidation' of nanoparticles, explaining the smaller oxidation signal recorded in anodic stripping voltammetry. This observation is crucially relevant to the use of anodic stripping voltammetry for the analysis of the nanoparticles. Further, the decrease in oxidative peak area provides a possible analytical method for melamine detection in solution.

Silver nanoparticles of varying degree of aggregation were oxidatively stripped from the electrode surface in order to study aggregation effects on anodic stripping voltammetry. Dopamine-capped silver nanoparticles were synthesised in different concentrations of melamine, which induces aggregation. Despite similar amounts of silver being drop cast on the electrode, the oxidation peak area under the voltammetric scan decreased with increasing melamine concentration. Hence, the decrease in oxidative peak area observed with increasing aggregation may be accounted for by the incomplete stripping of the silver nanoparticles. The incomplete stripping could arise from the two possible mechanisms of 'partial oxidation' and 'inactivation' (Scheme 3). In conclusion, the significant effects of aggregation must be noted when attempting to use anodic stripping voltammetry for the analysis or detection of nanoparticles.

Experimental Section

Reagents: NaNO$_3$ (>99.5%) was obtained from Fisons Scientific Equipment (Loughborough, UK). Dopamine hydrochloride (C$_8$H$_{11}$NO$_2$·HCl; 98.5%) was supplied from Alfa Aesar (Morecambe, UK). Melamine (C$_3$H$_6$N$_6$; 99%), AgNO$_3$ (>99%), and NaOH (≥98%) were obtained from Sigma–Aldrich, (Gillingham, UK). All solutions were made with ultrapure water from Millipore with resistivity no less than 18.2 MΩ·cm at 298 K.

Apparatus: All electrochemical experiments were performed with a three-electrode system in a Faraday cage with a water bath ther-

mostated at 26.0 ± 1.0 °C. The working electrode was a glassy carbon electrode obtained from CH Instruments, Inc. (Austin, USA). The diameter of the working electrode was 3.0 mm. The electrode was polished to a mirror finish with diamond sprays from Kemet International Ltd (Maidstone, UK) in the sequence of size 3.0 μm, 1.0 μm, and 0.1 μm. A standard mercury/mercurous sulfate electrode (MSE) ([Hg/Hg$_2$SO$_4$, K$_2$SO$_4$ (saturated)], +0.62 V vs. standard hydrogen electrode) was used.[12] The reference electrode was obtained from BASi (West Lafayette, USA). A platinum mesh (99.99%), obtained from Goodfellow Cambridge Ltd (Huntingdon, UK), was used as a counter electrode. A computer-controlled potentiostat, μAutolab III, from Metrohm Autolab BV (Utrecht, Netherlands) was used for electrochemical control and measurements.

Nanoparticle synthesis: The silver nanoparticles were synthesised using the method according to Ma et al.[8] C$_8$H$_{11}$NO$_2$·HCl (10 μL of 4.0 mm) and C$_3$H$_6$N$_6$ (10 μL of 0–1000 μm) were mixed in a centrifuge tube and left for 10 min. Ultrapure water (1.0 mL) was then added, followed by NaOH (10 μL of 0.10 m) and AgNO$_3$ (20 μL of 8.0 mm) to give a solution around pH 11. The centrifuge tube was wrapped in foil and left for 1 h. Dopamine reduces Ag$^+$ into Ag (Scheme 1). The solution was observed to turn from colourless to yellow, indicating the presence of silver nanoparticles.[8, 13] The resulting suspension was used for drop casting.

Preparation of the electrode modified with dopamine-capped silver nanoparticles: The nanoparticle suspension (3.0 μL) was drop cast onto a freshly polished glassy carbon electrode. The electrode was then dried under flowing nitrogen. The dry electrode was immediately used for the electrochemical experiments. For each experiment, a total of three repeats were carried out at 26.0 ± 1.0 °C.

Characterisation by UV/Vis spectroscopy: UV/Vis spectroscopy was carried out on a U-2001 spectrometer (Hitachi, Mannheim, Germany). A wavelength scan was performed from 700 nm to 250 nm at a rate of 400 nm min^{-1}. Tungsten iodide and deuterium light sources were used for the scans. Analysis was carried out on the nanoparticle suspension as synthesised, without further dilution. A surface plasmon signal around 418 nm was recorded, and this is a strong indication of the presence of silver nanoparticles.[13] This matches the colourimetric data obtained by Ma et al., where the maximum absorbance was around 410 nm.[8] In the presence of dopamine, it is evident that Ag$^+$ are reduced to form silver nanoparticles. Thus, the synthesis of dopamine-capped silver nanoparticles was considered successful.

Characterisation by scanning electron microscopy (SEM): As melamine is thought to bond with the quinone form of dopamine through either Michael addition or Schiff-base addition (Scheme 2 a,b), nanoparticles of varying degree of aggregation are produced with different melamine concentrations.[8, 10] Ma et al. have shown through transmission electron microscopy (TEM) that dopamine-capped silver nanoparticles aggregate in the presence of melamine.[8] The dopamine-capped silver nanoparticles were characterised using SEM. Secondary electron images were taken of the dopamine-capped silver nanoparticle synthesized at two different melamine concentrations, 1.0 μm and 1000 μm, using a Merlin scanning electron microscope (Zeiss, UK) at an acceleration voltage of 5.0 kV. Figure 3 shows that at a low concentration of melamine (1.0 μm), the sample has a smaller aggregated size compared with the nanoparticles synthesized at a high melamine concentration (1000 μm). Note that with the nanoparticles synthesized in higher melamine concentrations, more aggregation is observed. The average size of the dopamine-capped silver nanoparticle aggregates
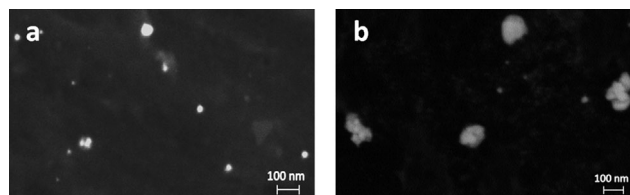
Figure 3. Scanning electron microscopy (SEM) images of dopamine-containing silver nanoparticles modified with different concentrations of melamine: a) 1 μm and b) 1000 μm.

synthesized with a low melamine concentration is ~37 ± 19 nm, and the average size with a higher melamine concentration is ~108 ± 55 nm.

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