

A proof-of-concept – Using pre-created nucleation centres to improve the limit of detection in anodic stripping voltammetry

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Abstract

Anodic stripping voltammetry is a much utilised method for trace metal analysis. We provide a simple proof-of-concept technique to improve the sensitivity of the method, which is illustrated by the detection of silver cations. This approach requires an electrode pre-treatment which involves drop casting a metal nanoparticle suspension and oxidising the nanoparticles, leaving small metal nuclei on the electrode surface. In turn, the small metal nuclei act as nucleation sites for subsequent metal deposition when used to interrogate target solutions. In particular, the pre-treatment increases the amount of deposited metal in a given amount of time. Silver nitrate concentrations from 30 nM to 1 μ M were tested and at silver ion concentration of 300 nM, the pre-treated electrode gave a signal which was 40 times larger than the untreated electrode. The larger signal leads to the enhancement of sensitivity and a lowering of the detection limit of anodic stripping voltammetry without introducing other organic molecules, metals or impurities.

1 Introduction

Anodic stripping voltammetry is a very well established technique for the detection of trace metals and sometimes other materials.^[1, 2] It is characterised by a high level of sensitivity coming from the pre-concentration of the target onto an electrode by reduction to the metallic form. The pre-concentrated metal is analysed by means of a positive going ('anodic') potential sweep. A similar approach is used in cathodic stripping voltammetry except that the target metal ions are typically concentrated as metal oxides rather than metals and the analysis is via a cathodic potential sweep.^[3-6]

The anodic stripping voltammetry technique can be optimised in various ways to allow for greater sensitivity or lower limits of detection. One obvious approach is to prolong the concentration step so as to enhance the amount of metal deposited. Note that because of the interplay of nucleation and growth, this is not necessarily a simple linear effect; in particular for progressive nucleation non-linear effects in time may be anticipated.^[7] A different approach is to modify the potential sweep so as to enhance the measurement sensitivity, for example, by replacing a linear sweep with a square wave or pulse voltammetric approach.^[8-13] Equally, the prevailing mass transport conditions can be enhanced to promote a greater flux of material to the electrode surface. In particular, the use of microelectrodes rather than macroelectrodes can increase sensitivity, as well as reproducibility of transport conditions, and the use of microelectrodes array is a further development.^[14-16] Alternatively, forced convection approaches can be utilised, of which sonovoltammetric methods are perhaps the best in terms of sensitivity enhancement.^[17-19] In addition, surface modification of electrode surface with organic molecules or other metals has been attempted to make the surface more favourable for metal deposition.^[9, 20-25]

In this paper, we present a proof-of-concept method of an alternative strategy for improving the sensitivity and limit of detection of anodic stripping voltammetry. Metal nanoparticles of the target metal are employed for an electrode pre-treatment procedure to provide nucleation centres in advance of the analysis of interest. A schematic diagram is provided in figure 1 to illustrate the concept. By pre-treating the electrode via depositing and stripping of metal nanoparticles, small metal nuclei

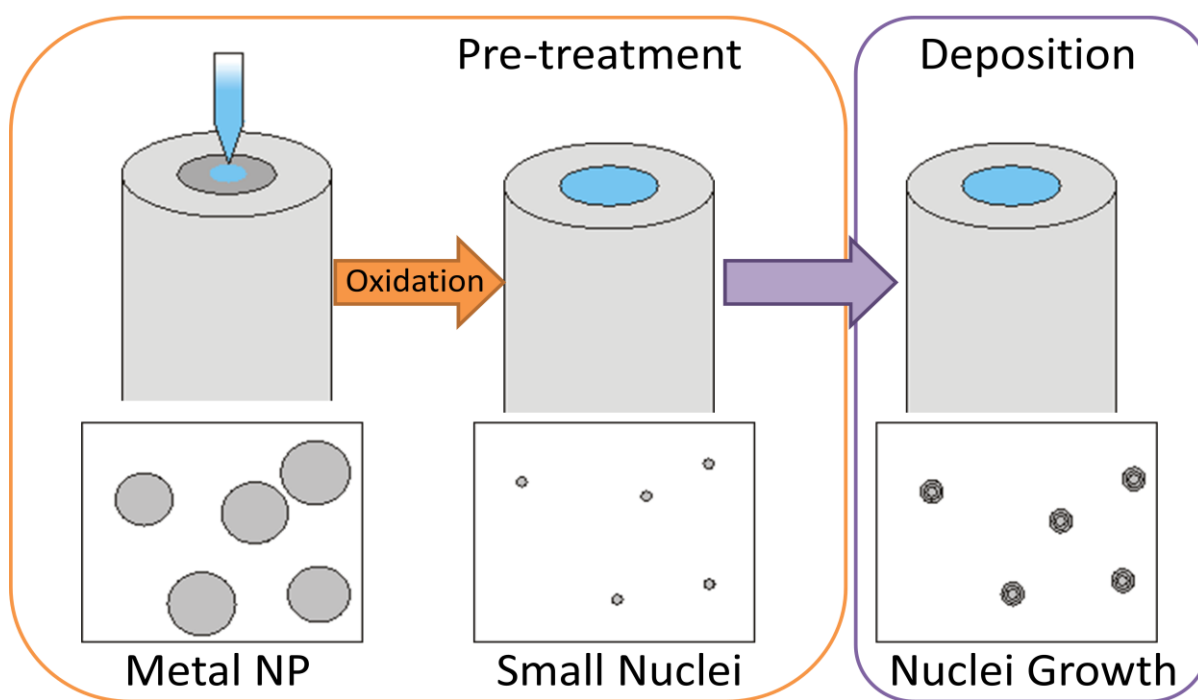


Figure 1. Schematic diagram of improving the limit of detection of anodic stripping voltammetry. Pre-treatment starts with drop casting of metal nanoparticles suspension onto the electrode surface which are then oxidised. Small metal nuclei are left behind from this pre-treatment and the pre-treated electrode is immediately used for deposition experiments. The metal ions in deposition experiment are deposited onto the small nuclei, resulting in nuclei growth and improved analytical sensitivity.

that are not detectable electrochemically are left behind on the electrode surface.^[26, 27] During the pre-concentration step of the anodic stripping voltammetry, these small metal nuclei then act as nucleation centres for metal ions of the same identity so as to enhance the deposition. Thus, more metal is deposited onto the electrode surface with the same pre-concentration duration as nucleation sites are already pre-created. This speeds up the deposition process because nucleation site formation can be a slow process that requires a high overpotential compared to metal growth.^[28] Hence, a larger peak charge can be measured within the same time frame with a pre-treated electrode as compared to an untreated electrode. The greatest advantage of this strategy lies in its simplicity. The pre-treatment only involves a simple drop casting of a metal nanoparticle suspension and then oxidising the

nanoparticles. No other foreign materials or impurities are introduced apart from the metal of interest. In this paper, silver is taken as an example to illustrate this proof-of-concept.

2 Experimental

2.1 Chemicals

Sodium nitrate (>99.5%, NaNO_3) was supplied by Fisons Scientific Equipment, Loughborough, UK. Trisodium citrate (>99%, $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$) was ordered from BDH Laboratory Supplies, Poole, UK. Silver nitrate (>99%, AgNO_3) and sodium borohydride (99%, NaBH_4) were obtained from Sigma-Aldrich, Dorset, UK. Concentrated nitric acid (>70%, H_2SO_4) and hydrochloric acid (~37%, HCl) were supplied by Fisher Scientific, Loughborough, UK. All solutions were made with ultrapure water from Millipore with resistivity not less than $18.2 \text{ M}\Omega\cdot\text{cm}$ at 298K.

2.2 Voltammetry

All electrochemical experiments were performed using a three electrode system in a Faraday cage with a $\mu\text{Autolab II}$ from Metrohm-Autolab BV, Utrecht, The Netherlands. The working electrode was a 3.0 mm diameter glassy carbon electrode from CH instruments, Austin, TX, USA. The electrode was polished to a mirror finish on diamond sprays in the sequence of size $3.0 \mu\text{m}$, $1.0 \mu\text{m}$ and $0.1 \mu\text{m}$ from Kemet, Kent, UK. A standard MSE (mercury/mercurous sulphate reference electrode ($\text{Hg}/\text{Hg}_2\text{SO}_4$, Hg_2SO_4 (saturated))), $+0.62 \text{ V}$ vs standard hydrogen electrode) from BASi, Wesly Lafayette, IN, USA.^[29] A platinum mesh functioned as the counter electrode. All measurements were performed at $25 \pm 1 ^\circ\text{C}$.

2.3 Silver Nanoparticle Synthesis and Characterisation

Silver nanoparticles capped with citrate were synthesised based on a method by Wan et al.^[30] In summary, 20 mL of 1% (w/v) trisodium citrate solution and 75 mL of ultrapure water was heated to $70 ^\circ\text{C}$ for 15 minutes. 1.7 mL of 1% (w/v) silver nitrate solution and 2 mL of freshly prepared 0.1% (w/v) sodium borohydride were added in quick succession to the heated solution. The mixture was stirred vigorously for another hour at $70 ^\circ\text{C}$. After cooling to room temperature, ultrapure water was

added to make the final volume of the nanoparticle suspension 100 mL. A clear yellow suspension of silver nanoparticles with a total silver concentration of 1mM was obtained. All glassware were cleaned thoroughly with aqua regia (a mixture of concentrated hydrochloric acid and concentrated nitric acid in 3:1 ratio) prior to silver nanoparticle synthesis.

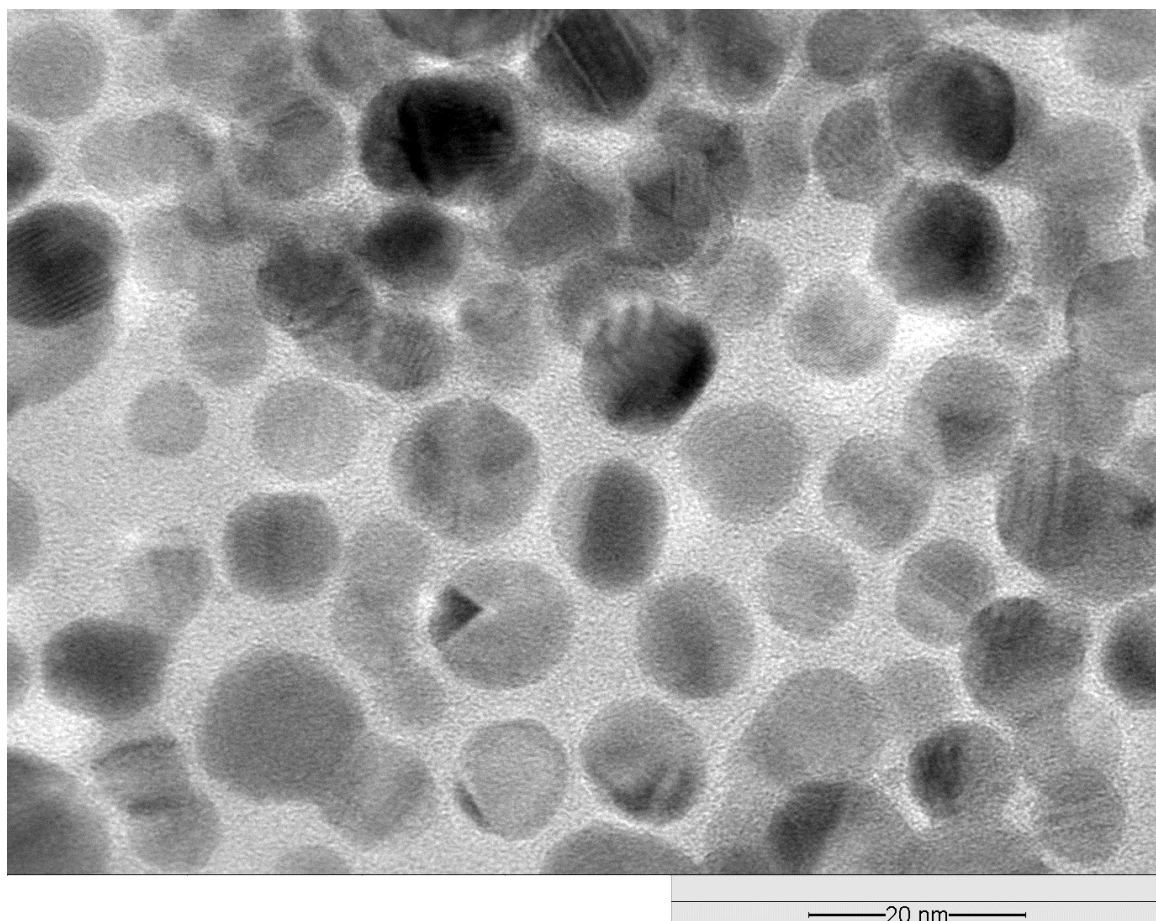


Figure 2. TEM brightfield image of silver nanoparticles. Mean radius of 4.7 ± 1.8 nm.

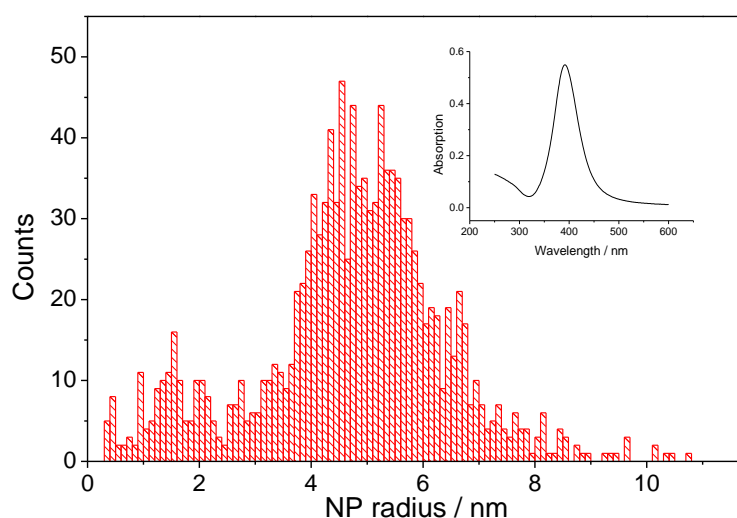


Figure 3. Size distribution of silver nanoparticles. Average radius of 4.7 ± 1.8 nm. Inlay: UV-vis spectrum of silver nanoparticles showing a distinct surface plasmon peak at 392 nm.

The characterisation of the silver nanoparticle suspension was performed by UV-vis spectroscopy (U-2001, Hitachi, Mannheim, Germany) and TEM (transmission electron microscope, FEI TECNAI T20, 200kV accelerating voltage, lanthanum hexaboride (LaB_6) filament). For UV-vis analysis, the nanoparticle suspension was diluted by a factor of 24 with ultrapure water. A wavelength scan from 600 nm to 250 nm at a scan rate of 400 nm min^{-1} was performed with a tungsten iodide and a deuterium light source. The surface plasmon peak is known to be affected by the size and shape of silver nanoparticles and the maximum absorption wavelength decreases with the nanoparticle size.^[31]
^[32] A surface plasmon peak at 392 nm was recorded and this indicated the presence of spherical silver nanoparticles smaller than a diameter of 29 nm.^[31] TEM was performed to measure the size of the nanoparticles. The nanoparticles represented in the TEM images were analysed with the software Image J (National Institutes of Health, USA). The areas of the clearly defined nanoparticles were measured and nanoparticle radii were calculated from the areas to take into account slightly non-spherical nanoparticles. A total count of 1223 nanoparticles gave a measurement of an average radius of 4.7 ± 1.8 nm. Figure 2 displays a TEM brightfield image of the silver nanoparticles. Figure 3 shows the size distribution of silver nanoparticles and the UV-vis spectroscopy measured.

2.4 Electrode Pretreatment Procedure

The glassy carbon electrode was pretreated, to deposit silver nuclei to enhance subsequent electrodeposition, using the following approach. First, nanoparticle modification of the glassy carbon electrode was carried out by drop casting 3 μL of the diluted silver nanoparticle suspension onto the electrode surface and drying the electrode under a flowing nitrogen atmosphere. The silver nanoparticle suspension had a total silver concentration of 1mM and was diluted by a factor of 500 before drop casting. Next, linear sweep voltammetry was performed with the modified electrode by scanning from -0.3 V to 0.2 V vs MSE. A signal was observed at around 0 V which corresponds to the oxidation of silver to silver ions.^[33] The linear sweep voltammetry removed most but not all of the silver cast. A second scan from -0.1 V to 0.5 V vs MSE was conducted and no silver oxidation signal was observable. The second linear sweep voltammetry began at a higher potential of -0.1 V instead of -0.3 V to ensure fresh silver ion generated from oxidation in the first scan did not deposit back onto the electrode, causing a false positive. The absence of signal in the second scan showed that any small metal nuclei left behind are not electrochemically detectable and the oxidation signal from the deposition experiments comes solely from the deposited silver. After the first linear sweep voltammetry, the electrode is considered as “pre-treated”. The electrode was rinsed in a vial of water and used for silver deposition experiment immediately.

3 Results and Discussions

In this section, pre-treated electrodes are shown to be more favourable for subsequent silver deposition as compared to a bare untreated glassy carbon electrode. In section 3.1, the proof-of-concept is presented with a deposition experiment with 300 nM of silver nitrate. In section 3.2, a range of silver nitrate concentrations are used in deposition experiments to display the effects of silver ion concentration on the amount of silver deposited.

3.1 Proof-of-Concept

Silver deposition experiments were performed on two types of electrodes – first a bare untreated glassy carbon electrode which was polished to a mirror finish and second on an electrode pre-treated

with the procedure described in section 2.4. On both electrodes, deposition of silver was performed at a potential of -0.4 V vs MSE for 15 minutes in a solution containing 300 nM of silver nitrate and 0.1 M sodium nitrate as the electrolyte. A stirring rate of 200 rotations per minute was maintained with a magnetic stir bar (25 mm in length) for deposition and stirring was switched off 2 minutes before the scan (after the first 13 minutes of deposition). Stirring was crucial to the experiment as it reproducibly delivered metal ions to the electrode surface and kept the diffusion layer thickness of the electrode to a minimum. Diffusion of the metal ions alone within the time of 15 minutes was insufficient to deposit substantial amount of metal onto the electrode surface for electrochemical analysis. Consequently, stirring during deposition ensures that the analysis can be performed within shorter timescales. Throughout the 15 minute deposition, silver ions were pre-concentrated and deposited as silver onto the working electrode. After that, an anodic stripping voltammetry starting from -0.3 V to 0.2 V and sweeping back to -0.6 V was performed at 0.05 V s^{-1} . A broad oxidative stripping peak was obtained at around 0 V vs MSE and the charge underneath the signal was measured to determine the amount of silver deposited upon the surface. The voltammogram obtained from deposition experiments with electrolyte containing 300 nM of silver nitrate for both the bare untreated glassy carbon electrode and the pre-treated electrode are plotted in figure 4. As observed, the silver stripping signal of the pre-treated electrode is larger than the untreated electrode. Upon closer inspection, the amount of silver deposited on a pre-treated electrode is ca. 40 times greater than a bare untreated glassy carbon electrode. Although the electrodes used in the pre-treated and untreated experiments were both glassy carbon electrodes, it is concluded that the pre-treatment provided small amounts of silver clusters on the electrode surface. These clusters improved the signal of the pre-treated electrode by providing pre-existing nucleation centres for immediate deposition of silver, where for the untreated electrodes, nucleation must occur before deposition can take place. Within the literature, silver has been known to deposit at a lower potential when nucleation centres are present.^[28] In the literature, TEM images showed that electrochemical oxidation via a linear sweep voltammetry is insufficient to remove all the silver drop cast or deposited and that the small nuclei were relatively stable and removed completely only when an overpotential of 500 mV vs Ag/Ag^+ is maintained for a duration of more than an hour.^[26, 27] Thus, the pre-treatment is inferred to have left sufficient

nucleation centres for more silver to be deposited onto the electrode surface during the 15 minutes deposition period, leading to a greater peak charge. Consequently, this provides a possible route

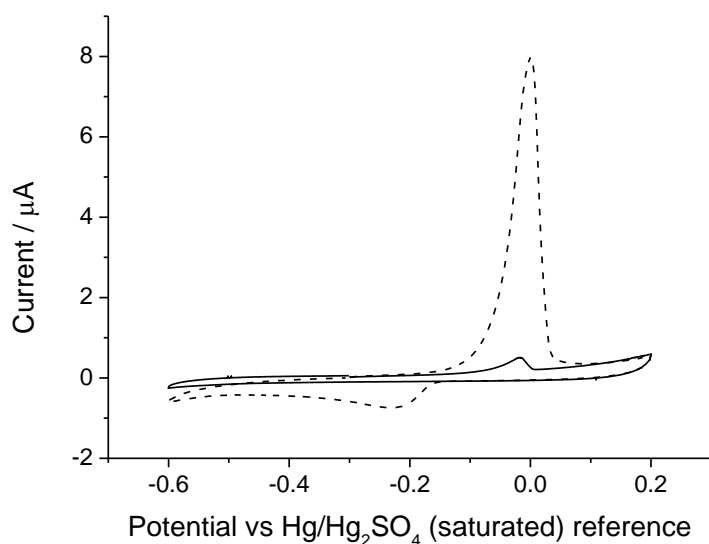


Figure 4. The oxidative stripping of silver from a glassy carbon electrode after deposition at -0.4 V vs Hg/Hg₂SO₄ (saturated) reference electrode for 15 minutes in 0.1 M sodium nitrate spiked with 300 nM of silver nitrate at a scan rate of 0.05 V s⁻¹. Stirring at 200 rotations per minute was maintained for the first 13 minutes of the deposition. Solid line: Bare untreated glassy carbon electrode. Dashed line: Pre-treated glassy carbon electrode.

for lowering the detection limit of anodic stripping voltammetry. Moreover, in the next section, the experiment was repeated with various silver nitrate concentrations to further develop this idea.

3.2 Response at Different Silver Nitrate Concentrations

Deposition experiments with pre-treated electrodes and bare untreated glassy carbon electrodes were performed at 7 different concentrations of silver nitrate. The silver nitrate concentrations tested were 30 nM, 50 nM, 100 nM, 200 nM, 300 nM, 600 nM and 1 μ M. Identical parameters were used as the ones in the experiments above in Section 3.1. Figure 5A depicts the peak charge measured at various

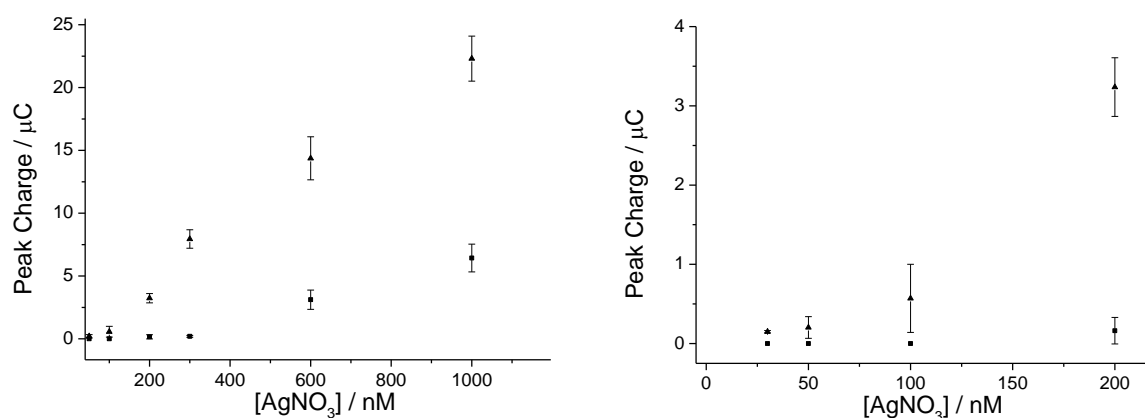


Figure 5A. The oxidative stripping of silver from a glassy carbon electrode after deposition at -0.4 V vs Hg/Hg₂SO₄ (saturated) reference electrode for 15 minutes at a scan rate of 0.05 V s⁻¹. Deposition was performed in 0.1 M sodium nitrate spiked with different concentrations of silver nitrate (30 nM, 50 nM, 100 nM, 200 nM, 300 nM, 600 nM and 1 μ M). Stirring at 200 rotations per minute was maintained for the first 13 minutes of the deposition. The peak charge of the voltammetric signal is plotted against the concentration of silver nitrate. Each data point consists of a minimum of 3 repeats. Squares: Bare untreated glassy carbon electrode. Triangles: Pre-treated glassy carbon electrode. Figure 5B. A close up of figure 5A.

concentrations of silver nitrate with a pre-treated electrode or a bare untreated glassy carbon electrode. Figure 5B is a close up of figure 5A for the lower concentration range. At silver nitrate concentrations equal or less than 100 nM, there was no signal recorded for silver oxidation for a glassy carbon electrode without pre-treatment. However, at all concentrations of 30 nM to 1 μ M of silver nitrate, a

silver oxidation signal, which is *at least* three times larger than the untreated electrode, was observed for the pre-treated electrode.

As seen in both figure 5A and 5B, the relationship between measured peak charge and silver nitrate concentration is not linear despite the trend of increasing peak charge with increasing silver nitrate concentration. During the deposition period, there are two main processes of nucleation and growth. Nucleation refers to formation of a ‘seed’ on the electrode surface while growth refers to the additional deposition of silver onto the ‘seed’. Nucleation requires a higher overpotential than growth.^[28] The presence of existing nucleation centres speeds up the process of growth since nucleation is no longer essential. Hence, the difference in rate for both processes accounts for the non-linear trend observed cross the various silver nitrate concentrations. Accordingly, given that signal

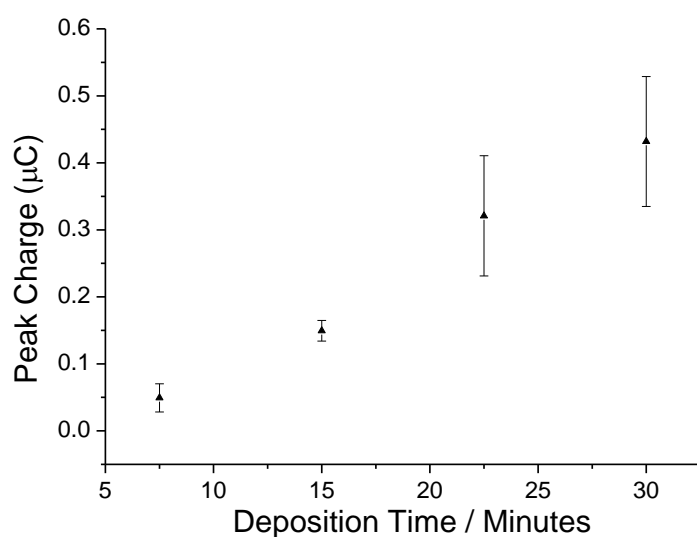


Figure 6. The oxidative stripping of silver from a pre-treated glassy carbon electrode after deposition at -0.4 V vs Hg/Hg₂SO₄ (saturated) reference electrode for various time frames in 0.1 M sodium nitrate spiked with 30nM of silver nitrate at a scan rate of 0.05 V s⁻¹. Stirring at 200 rotations per minute was maintained during deposition and switched off 2 minutes prior to the scan. The peak charge of the voltammetric signal is plotted against the deposition time. Each data point consists of a minimum of 3 repeats.

amplification is observed with the pre-treated electrode, detection of silver ions at a much lower concentration is possible.

To further lower the detection limit, the deposition time can be altered. When the deposition time is extended, more time is given for the growth process and at a lower concentration of silver nitrate, a larger signal is recorded and the detection limit lowered. Thus, more experiments with different deposition time were performed (see figure 6). With a silver nitrate concentration of 30 nM, the pre-treated electrode underwent various deposition time of 7.5, 15, 22.5 and 30 minutes. Similar to the experiments reported in section 3.1, a stirring rate of 200 rpm was maintained and switched off 2 minutes before the voltammetric scan. This meant that the stirring was sustained for 5.5, 13, 20.5 and 28 minutes respectively. The oxidation of deposited silver on electrode surface gave a signal and the peak charge was measured and plotted against deposition time to give figure 6. Figure 6 shows that with increasing deposition time, more silver deposit onto the electrode surface and the peak charge measured increases. Hence, smaller concentrations of silver ions can be detected when deposition time is prolonged.

4 Conclusions

Anodic stripping voltammetry is a very common method of quantifying the amount of metal ions in solution and within the literature, many studies have been attempted at lower the detection limit by adding organic molecules or other metals.^[9, 20-25] This paper aims to provide a simple proof-of-concept, where the detection limit can be lowered without complicated pre-treatment or modification, illustrated for the case of silver deposition. By pre-treating the electrode, small silver clusters, not detectable by electrochemical means but their presence are confirmed by TEM, can be formed and act as nucleation centres for the subsequent deposition of silver and amplify the signal obtained from anodic stripping voltammetry of silver. The pre-treated electrode gave a signal which is at least three times larger than the bare untreated glassy carbon electrode across the concentration range of 30 nM to 1 μ M of silver nitrate. At 300 nM of silver nitrate, there is a 40 fold increase of the peak charge with pre-treated electrode compared to the bare glassy carbon electrode. The peak charges measured

underneath the signals follow an increasing but non-linear trend with increasing silver nitrate concentrations because both nucleation and growth occur simultaneously. Finally, to further lower the detection limit, the deposition time of silver can be extended.

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