Nanoparticle impacts show high ionic strength citrate avoids aggregation of silver nanoparticles

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To date the use of particle coulometry for the quantification and sizing of silver nanoparticles has been hindered due to in-situ agglomeration/aggregation. Four different batches of silver nanoparticles are synthesised with mean diameters ranging from 17 to 46 nm and are studied using particle coulometry. By utilising tri-sodium citrate as an electrolyte agglomeration/aggregation is all but eliminated over the time scale of the impact experiments. Consequently, the electrochemical impact methodology is demonstrated to fully and quantitatively describe the nanoparticle size distribution.

With the advancement of nanotechnology, the application of nanoparticles in diverse commercial and industrial products is increasing.[1] Concurrently, there is a growing demand for rapid and accurate analytical detection and quantification methodologies.[2] For the modern chemist there are a wide variety of nanoparticle analytical techniques available, all of which exhibit their own distinct advantages and disadvantages.[3] A new detection methodology utilises the stochastic detection of nanoparticles through their anodic dissolution at an electrochemical interface.[4,5] A suitable micro-electrode is submerged into a solution containing electroactive nanoparticles. Due to Brownian motion the nanoparticles will sporadically collide with the electrochemical interface. Assuming a suitably oxidative potential is held upon the electrode then, upon impact, a Faradaic current will be passed corresponding to the total oxidation of the impacting particle.[6] By electrochemically monitoring these impact events and recording the the total charge passed during the collisions the quantity of material and hence the size of the nanoparticle may be measured (via the use of Faraday's first law).

Previous particle coulometry investigations of silver nanoaprticles have been complicated by the in-situ agglomeration/aggregation of the nanoparticles.[7,8] This arises due to the requirement of relatively high ionic strengths in the electrochemical set-up. Conversely, in this article we report the use of high concentrations of citrate as an electrolyte and nanoparticle stabilising agent which all but eliminates the problem of agglomeration/aggregation. The synthesis and electrochemical characterisation of a range of nanoparticle distributions is undertaken and it is demonstrated that the obtained electrochemical results are in agreement to those measured independently from scanning electron microscopy (SEM).

Citrate-capped silver nanoparticles (Ag NPs) of four different sizes (Batches I-IV) were synthesised following a stepwise seeded growth method developed by Wan et al.[9] Further information regarding this synthesis procedure can be found in the SI section 1. The shape and size of the different NP batches were characterised by high-resolution SEM (Leo Gemini 1530, Zeiss). Each Ag suspension was drop cast onto a TEM grid modified

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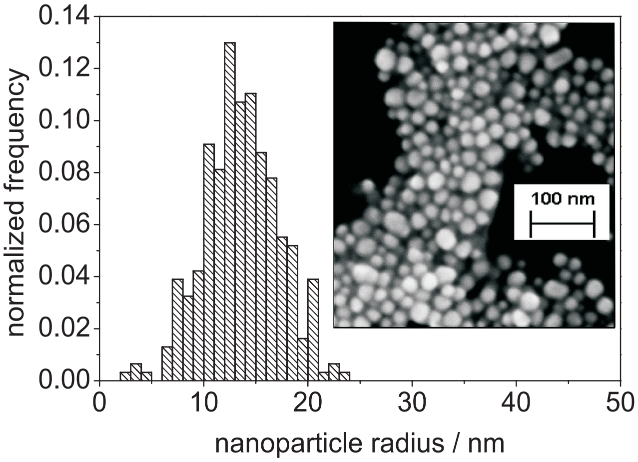

Fig. 1 Size distribution of Batch II Ag NPs as derived from SEM analysis, inlay shows a representative SEM image showing the nanoparticles size and spherical shape.

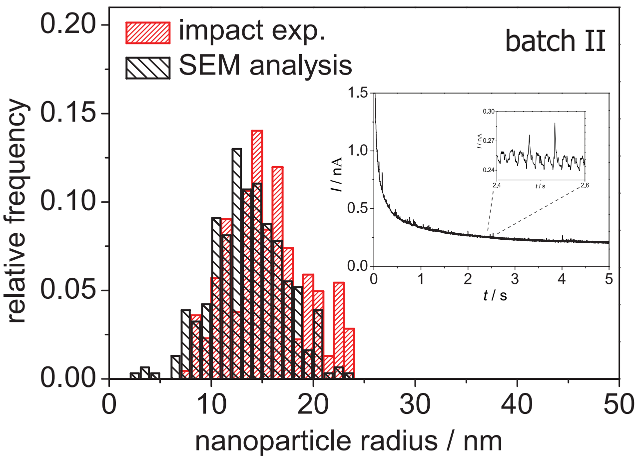

Fig. 2 Ag NP size distribution derived from impact experiments (red columns) and SEM analysis (black columns) for Ag NP batch II; the inlay shows a representative chronoamperogram and the associated NP impact spikes for the same batch in 0.1M tri-sodium citrate.

SEM holder to minimise agglomeration of the nanoparticles. The obtained SEM images were analysed to determine the particle size distribution for each batch using the software imageJ (National Institutes of Health). Figure 1 depicts the normalised characterisation data for the Batch II Ag nanoparticles. From this SEM data the mean radius and standard deviation of Batch II was determined to be 13.6±3.7 nm. The full SEM characterisation for the other three batches can be found in the SI section 2.

Electrochemical impact experiments were performed in a 0.1 M $Na_3C_6H_5O_7$ (tri-sodium citrate) solution in a three electrode setup at room temperature employing a μAutolab II potentiostat (Metrohm-Autolab BV, Utrecht, Netherlands). A carbon fibre micro electrode (ø= 10μm) was used as the working electrode (WE) and a graphite rod served as the counter electrode. All potentials were applied against a silver wire pseudo-reference electrode or a saturated mercury (I) sulphate [$Hg/Hg_2SO_4, K_2SO_4$(sat.)] reference electrode (MSE, E^o= +0.650V vs NHE).

For the impact studies the carbon micro-electrode was stepped to a suitably oxidising potential (+0.3V vs Ag or +0.6V vs MSE) and held there for 5 seconds. Multiple repeats were performed such that the total number of recorded impact events per batch was greater than 100. The recorded current response for all of the nanoparticle batches showed impact spikes and, as anticipated, the average spike area was found to increase with increasing size of the silver nanoparticles in each batch. Figure 2 depicts both the resulting size distributions obtained from analysis of the impact data and the SEM analysis for Batch II. The NP's mean radius and standard deviation for Batch II as determined from the impact data was found to be 15.5±3.8 nm, which is in excellent agreement with that found from the SEM analysis.

Comparison of the Ag NP size distributions determined by SEM and impact experiments for the other three batches are visualised in Figure 3 and the derived mean radii and standard deviations are summarised in Table 1. Importantly, for the impact data the raw size distribution obtain from the analysis of the impact spikes has been weighted so as to account for the lower probability of the larger nanoparticles colliding with the electrode. The origins of this weighting can be understood

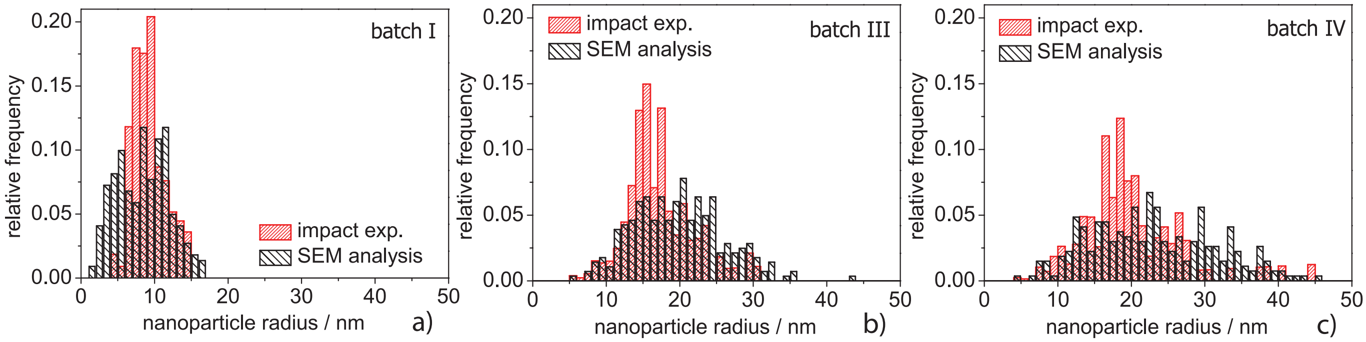

Fig. 3 Comparison of the Ag NP size distributions derived from impact experiments (red) and SEM analysis (black) for a) batch I, b) batch III and c) batch IV.

through consideration of the general equation describing the steady-state diffusion only flux (j_{ss}) to a microelectrode,[10]

$$j_{ss} = \frac{4D_i[i]}{\pi r_0} \tag{1}$$

where D_i is the diffusion coefficient of species i ($m^2\ s^{-1}$), $[i]$ is the concentration of species i (mol m^{-3}) and r_0 is the radius of the electrode (m). The diffusion coefficient for nanoparticles of this size may be described through the use of the Stoke-Einstein equation for suitably large nanoparticles ($r \geq 5$nm).[11,12] Consequently, the diffusion coefficient for a nanoparticle is inversely proportional to its radius. Therefore, from Equation 1 it can be concluded that for a given concentration the frequency and therefore the probability of the nanoparticles impacting the electrode scales inversely with the radius. To account for the fact that smaller particles diffuse faster and hence impact more frequently the raw impact data must be weighted with the inverse of the diffusion coefficient. Due to the relatively narrow nanoparticle distributions this weighting is found to minimally alter the obtained size distributions, as evidenced in the SI section 3.

From the comparison between the SEM and impact data it can be concluded that both sizing methods are in very good agreement throughout the range of investigated NP sizes. This observation indicates that in contrast to previous impact analyses performed in chloride-containg electrolytes,[7,8] no significant agglomeration - over the time frame of the experiments - of the Ag nanoparticles in the 0.1M tri-sodium citrate electrolyte is observed, rendering this a useful methodology for studying the size distribution of Ag nanoparticles in aqueous media.

Table 1 Summary of the derived mean radii (r) and standard deviation (σ) for the different nanoparticle batches as measured from SEM and electrochemical impact analysis.

Batch	SEM /nm	Impact /nm
I	8.5±3.5	9.2±2.2
II	13.6±3.7	15.5±3.8
III	19.8±6.2	17.2±4.4
IV	23±8.6	19.9±6.2

From inspection of Figure 3 a) it can be seen that for small nanoparticle radii (≤6nm) there is a discrepancy between the SEM and impact size distributions. This may be understood through consideration of the lower size limit of detection for the impact methodology. The shortest recorded impact spikes have a duration of approximately 3 milliseconds, assuming that the smallest event that can be measured has a height of twice that of the electrochemical noise (for the Batch I experiments the noise was found to be of the order of 2-3pA) then approximating the impact spike as being a simple right angle triangle, the minimum measurable nanoparticle size is found to be approximately 6 nm in radius.

In conclusion, this work has demonstrated that particle coulometry with the use of high concentrations of citrate as both an electrolyte and nanoparticle stabilising agent allows the accurate and quantitive analysis of the size distribution of silver nanoparticles (with mean radii ranging from 8.5-23 nm) without the complication of of agglomeration/aggregation.

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