

## Materials Chemistry

## Nanoparticle Capping Agent Controlled Electron-Transfer Dynamics in Ionic Liquids

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**Abstract:** Herein, we report a change in the mechanism of the oxidation of silver nanoparticles (Ag NPs) with the molecular weight of a poly(ethylene) glycol (PEG) capping agent. Characterisation of the modified nanoparticles is undertaken using dynamic light scattering and UV/Vis spectroscopy. Electrochemical analyses reveal that the oxidation of 6000 molecular weight (MW) PEG is consistent with a poly-

mer-gated mechanism, whilst for 2000 MW PEG the polymer does not hinder the oxidation. The 10,000 MW PEG Ag NPs are rendered almost electrochemically inactive. This study demonstrates the ability to alter and better understand the electron-transfer mechanism in a room temperature ionic liquid (RTIL) by systematically altering the capping agent.

## Introduction

Interest in the fundamental properties of nanomaterials has increased rapidly with their inclusion in consumer products. Their use in products ranges from sports apparel, to large home appliances and medical implants. This is especially true for nanosilver due to its purported antimicrobial advantages over bulk silver.<sup>[1–3]</sup> Of particular interest is the affect of the capping agent, which is used to stabilise the nanoparticle, and alter its properties and behaviour.<sup>[4]</sup>

A number of studies have been undertaken in aqueous solvents to attempt to gain a deeper understanding of changes in dynamics as a result of a change in the capping agent.<sup>[4,5]</sup> Poly(ethylene) glycol (PEG), a molecule that is used as a capping agent because of the steric hindrance it provides, is selected as the capping agent of choice in a wide range of applications.<sup>[6]</sup> In the medical field, the length of the PEG chain has been manipulated in a range of studies,<sup>[7–9]</sup> and, for example, can affect the nanoparticle's uptake into cells, and reduce macrophage interception.<sup>[10]</sup> The molecular weight of the PEG capping agent has also been shown to strongly influence plasma protein adsorption, and, therefore, how long nanoparticles are able to persist in the bloodstream.<sup>[11]</sup>

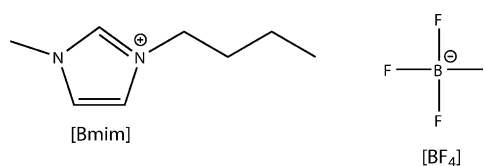
Thus far, much of the fundamental analysis into nanoparticle dynamics has been undertaken in aqueous solvents, with studies into the characterisation of the nanoparticle's size,<sup>[12]</sup> tendency to aggregate,<sup>[13]</sup> and concentration.<sup>[14]</sup> Although changes in the capping agent are, as detailed above, understood to

affect the dynamics of the nanoparticle, the studies undertaken in aqueous media have failed to establish a difference in electron-transfer behaviour.<sup>[15]</sup>

This lack of understanding, combined with the fact that there is sustained interest in developing a fundamental knowledge base of nanoparticle behaviour, and, in particular, the role of the capping agent, in high ionic strength media (for example, bodily fluids), encouraged us to examine nanoparticle dynamics in a room temperature ionic liquid (RTIL) as it may provide valuable insights.

RTILs are molten salts at room temperature that consist of an inorganic anion and a bulky, asymmetric cation.<sup>[16,17]</sup> They have a number of desirable properties that make them highly suitable as electrochemical solvents—among these properties are their large electrochemical windows,<sup>[18]</sup> recyclability, and tunability<sup>[19]</sup> due to the ability to customise the RTIL for purpose with respect to physicochemical properties (such as hydrophilicity, miscibility, and viscosity). The ionic liquid chosen in this study is 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>], Figure 1) selected for its miscibility with water and the ease of its synthesis.

Silver nanoparticles have recently been examined in the above RTIL,<sup>[20]</sup> and this work revealed that the oxidation of 5000 MW PEG-capped silver nanoparticles (Ag NPs) proceeds by a different mechanism in a RTIL as compared with water. In water, spikes in the current correspond to a silver nanoparticles undergoing oxidation after diffusing to the electrode through



**Figure 1.** The RTIL used in this study: 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>]).

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Brownian motion and coming into electrical contact directly upon arrival.<sup>[12,21]</sup> A “polymer-gated” mechanism was proposed in the RTIL, whereby nanoparticles accumulate at the electrode surface and undergo a reversible “unwrapping” process, before irreversible oxidation once the silver core becomes accessible for electron transfer.

Given that it is likely modification of the capping agent will result in a change in dynamics, undertaking a systemic study of the affects of modifying the PEG capping agent will allow insight into the microscopic and nanoscopic interactions, and provide more information about the polymer-gating mechanism previously proposed. This study provides an experimental investigation into the role of the capping agent in affecting the dynamics of electron transfer of Ag NPs in a RTIL demonstrating the critical role the capping agent plays in the mechanism of electron transfer.

## Experimental Section

### Chemical reagents

Poly(ethylene glycol) methyl ether thiol (thiolated PEG, MW 2000 and 6000, Sigma Aldrich) and poly(ethylene glycol) methyl ether thiol (thiolated PEG, MW 10,000, Nanocs Inc, Boston, USA) were used as received. Where water is referred to, ultrapure water from Millipore with resistivity of not less than 18.2 MΩ cm at 25 °C was used. The citrate-capped 20 nm diameter silver nanoparticles<sup>[22]</sup> were prepared by standard literature methods, and sized by SEM as 8.5 ± 3.5 nm in radius. The 1-butyl-3-methylimidazolium tetrafluoroborate ([Bmim][BF<sub>4</sub>]) was also prepared according to standard literature methods.<sup>[19]</sup> Argon (99.5%), for use with the Glovebox, was purchased from BOC, Surrey, UK.

### Nanoparticle modification

In each case, a small amount of solid thiolated PEG (2.4 mg, 2.2 mg, 3.2 mg in the case of 2000, 6000, and 10,000 molecular weight PEG respectively) was dissolved in 1 mL of water. To replace the citrate capping with a PEG of appropriate length, 10 μL of the thiolated PEG stock solution was combined with 490 μL of the citrate-capped Ag nanoparticles, shaken, and left undisturbed for 30 mins, during which time the solution turned from a pale into an intense yellow colour. This was repeated for each molecular weight of PEG.

### Dynamic light scattering

Dynamic light scattering (DLS) measurements were performed using a Malvern Zetasizer Nano ZS instrument to measure the hydrodynamic radius of the nanoparticles (capped with citrate, and 2000, 6000, and 10,000 MW PEG). Each sample was diluted (50 μL of nanoparticle solution in 1 mL of water) and filtered, using a sterile Whatman 0.2 μm filter to remove any dust particles or other large contaminants, before being placed in a disposable solvent-resistant microcuvette. Before any measurements were taken, the sample was equilibrated at 25 °C inside the DLS instrument for two minutes. Three sets of twelve light scattering measurements were then taken using 570 nm light, and averaged to give three size distributions for the nanoparticles.

### Transfer into ionic liquid

The nanoparticles were successfully transferred from water into the RTIL, as evidenced by UV/Vis spectrophotometry, by combining 2 μL of the modified silver nanoparticle solution with 30 μL of RTIL. This produced a final concentration of 4.6 × 10<sup>-7</sup> mol m<sup>-3</sup> Ag NPs. The solution was then placed under a 0.2 mbar vacuum overnight to remove residual water.

### UV/Vis spectroscopy

UV/Vis spectrophotometry was recorded on a Shimadzu UV-1800 using 50 μL High Precision Quartz Cells (Hellma Analytics, Germany). In all cases, a baseline correction was performed with empty cells inside the instrument prior to measurement, and the absorbance was recorded from 1100–250 nm. For the experiments conducted in water, each sample was diluted prior to analysis by combining 10 μL of the nanoparticle solution with 210 μL of water, and water was used as the reference solvent. For the experiments undertaken in RTIL, 10 μL of the nanoparticle solution was combined with 70 μL [Bmim][BF<sub>4</sub>], and placed under vacuum overnight. An additional 70 μL aliquot of neat RTIL was placed under vacuum, and this sample was used in the reference cell.

### Transfer into glovebox and electrochemical assembly

All electrochemical experiments were carried out in an acrylic MBRAUN glovebox (GB-2202-P-VAC) under an inert argon atmosphere. Before initial use, the glovebox was purged in totality a dozen times and items entering the glovebox after this initial period were transferred through the antechamber, which went through three purge and refill cycles prior to their introduction to the main chamber. Once all of the samples had been brought into the glovebox, a solution containing 10 μL of the NP in RTIL stock solution was placed in a plastic collar fixed on top of the working electrode, and a T-cell was used for structural stability, as described previously.<sup>[23]</sup>

### Electrochemical apparatus

Electrochemical experiments (cyclic voltammetry and chronoamperometry) were conducted using a low noise potentiostat that was built in-house and has been described in full previously.<sup>[20,24]</sup> All experiments were conducted inside a temperature-controlled Faraday cage.<sup>[25]</sup> The working carbon microdisc electrode (IJ Cambria Scientific Ltd, UK), 7 μm nominal diameter, was polished prior to use using a water-alumina slurry (1, 0.3, 0.05 μm, five minutes on each grade) on soft lapping pads (Buehler, Illinois).<sup>[26]</sup> The precise radius was determined through calibration of the electrode with a 2.0 mM solution of ferrocene in acetonitrile containing 0.1 M tetra-*n*-butylammonium perchlorate (TBAP) (silver wire as both a counter and quasi-reference electrode); chronoamperometry was recorded at 298 K, and assuming a diffusion coefficient of 2.3 × 10<sup>-9</sup> m<sup>2</sup> s<sup>-1</sup>,<sup>[23]</sup> the data was analysed with respect to the Shoup and Szabo equation.<sup>[27]</sup> This gave an electrode radius of 3.55 ± 0.05 μm. A 0.5 mm silver wire was used both as a counter and a quasi-reference electrode in all experiments.

## Results and Discussion

This section outlines the modification and subsequent characterisation of silver nanoparticles in water using DLS and UV/Vis spectrophotometry. This is followed by transfer of the PEG-capped NPs (2000, 6000, and 10,000 MW) into [Bmim][BF<sub>4</sub>],

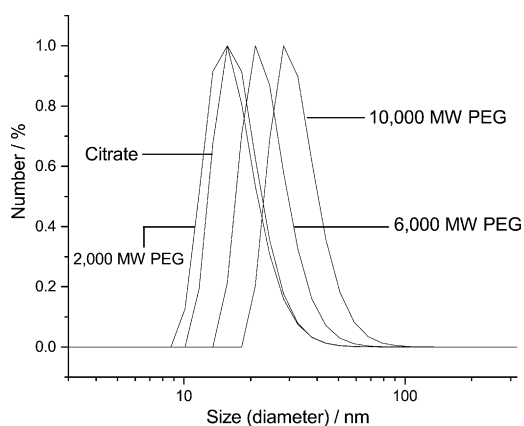
which was also characterised using UV/Vis spectrometry. Finally, electrochemistry was undertaken in the form of chronoamperometry on the samples, the outcome of which is sizing of the nanoparticles, and insight into the mechanism of oxidation.

### Modification of nanoparticles

The silver nanoparticles capped with citrate were recapped with poly(ethylene) glycol of increasing molecular weights (2000, 6000, 10,000) before any analysis was undertaken. This was achieved by combining dissolved samples of thiolated PEG in water with citrate capped nanoparticles, mixing the samples thoroughly, and allowing the capping agent replacement to occur over a period of 30 minutes. Two analysis techniques were undertaken to monitor this modification, which will be outlined below. UV/Vis was also used to monitor the transfer of modified nanoparticles from water into a RTIL so that electrochemical analysis could be undertaken.

### Dynamic light scattering

DLS was used to track the recapping of the nanoparticles with the variously weighted PEG molecules by monitoring the size of the nanoparticles' hydrodynamic radius. The analysis, shown in Figure 2, returned hydrodynamic radii (Z-averages) of  $29.3 \pm 0.1$  nm for the unmodified, citrate capped nanoparticles,  $29.7 \pm 0.4$  nm for the nanoparticles recapped with 2000 MW PEG,



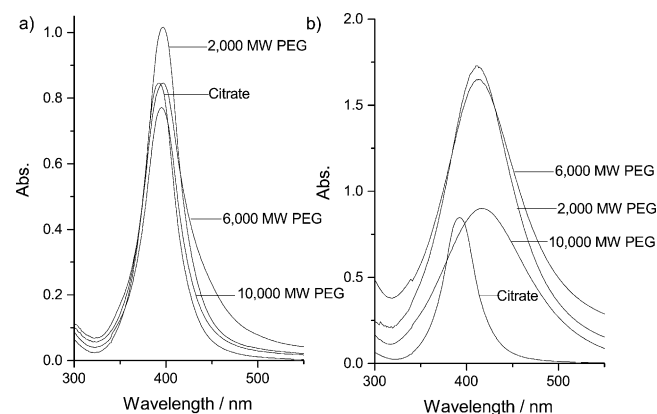
**Figure 2.** Normalised DLS analysis of citrate-capped Ag NPs, 2000 MW PEG-capped Ag NPs, 6000 MW PEG capped Ag NPs, and 10,000 MW PEG-capped Ag NPs.

$37.3 \pm 0.4$  nm for the 6000 MW recapped sample, and  $51.7 \pm 0.1$  nm for the 10,000 MW PEG Ag NPs. The Polydispersity Index (PDI) for all measurements was  $\leq 0.2$ , indicating that the sample was monodispersed. The hydrodynamic radii provide a measurement of the combined thickness of the capping agent layer and the core size. As the molecular weight of the PEG molecule increases, there is a significant increase in the observed size of the nanoparticle. This suggests that the modification was successful, and that the PEG chains are not simply

binding more tightly in the case of the larger molecular weights, allowing insight into the affect of a thicker capping agent layer on the electron-transfer kinetics.

### UV/Vis spectrometry

UV/Vis spectrophotometry was used to examine the plasmon peak resonance of the silver nanoparticles, which has been previously reported to be at 400 nm for PEG-capped silver nanoparticles in water.<sup>[20]</sup> A shift or absence of the plasmon peak can indicate that aggregation or dissolution has occurred,<sup>[20]</sup> and so UV/Vis spectrometry is a reliable method of establishing that nanoparticles remain in solution. In water, the citrate capped nanoparticles reached their maximum absorption at 392 nm, whilst all three of the PEG-capped nanoparticles absorbed maximally at 396 nm. Although small, this nevertheless clear shift provides further evidence for the successful recapping of the nanoparticles (Figure 3).



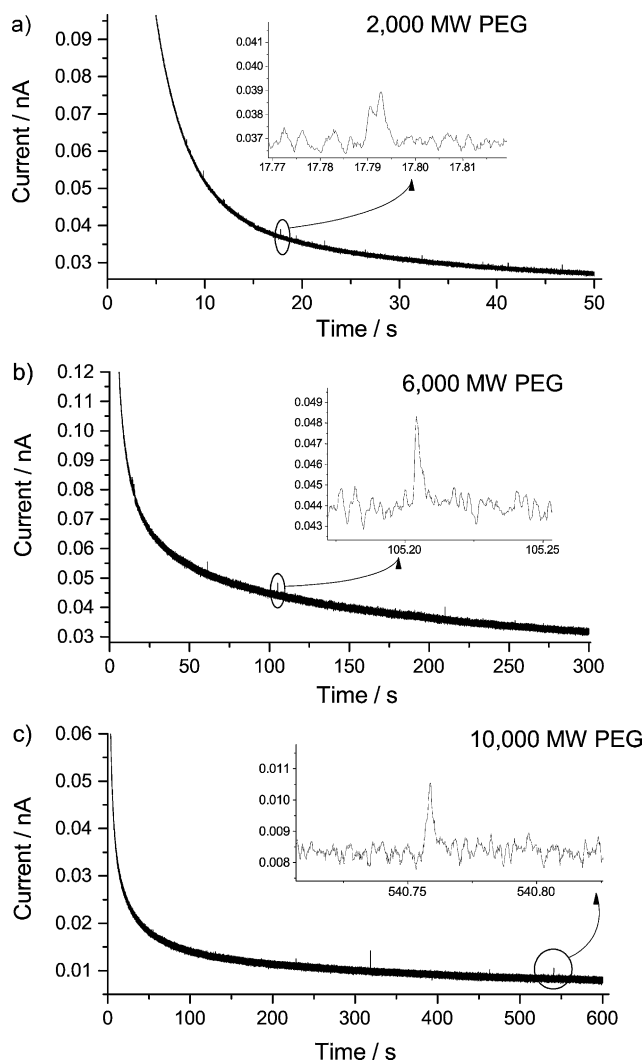
**Figure 3.** UV/Vis spectra of a) citrate, 2000, 6000, and 10,000 MW PEG-capped silver nanoparticles in water, at a concentration of  $3.0 \times 10^{-7} \text{ mol m}^{-3}$  and b) citrate capped in water for comparison with 2000, 6000, and 10,000 MW PEG-capped silver nanoparticles in [Bmim][BF<sub>4</sub>] at a concentration of  $9.3 \times 10^{-7} \text{ mol m}^{-3}$ .

In ionic liquid, the plasmon becomes much broader than the plasmon observed in water, and the maximum absorbance occurs at 412 nm. The existence of a plasmon peak in the IL provides evidence for the successful recapping and transfer into RTIL. In contrast, the UV/Vis spectrometry of citrate capped Ag nanoparticles, or lack thereof, has been reported previously,<sup>[20]</sup> which demonstrates that the citrate-capped NPs are not stable in an ionic liquid environment.

### Electrochemistry

The nanoparticles solvated in the ionic liquid, still under vacuum, were transferred into a glovebox, and an aliquot (10  $\mu\text{L}$ ) of 2000 MW PEG in RTIL was placed onto a microcarbon working electrode (of radius 3.55  $\mu\text{m}$ ), with a silver wire as a counter and pseudo-reference electrode also immersed. The use of a pseudo-reference electrode may result in a variation in potential necessary to observe oxidation, and the potential

was varied ( $\pm 0.1$  V) in the subsequent experiments to reflect this possibility. Chronoamperometry was then performed by holding the potential at 1.7 V for 50 s. Upon application of a sufficiently positive potential, spikes in the current appear during the course of the chronoamperogram. A series of chronoamperograms were recorded in order to obtain a sufficient number of spikes for analysis. This procedure was repeated with the nanoparticles capped with 6000 and 10,000 MW PEG, holding the potential at 1.7 V for 300 s and at 1.6 V for 600 s, respectively. Figure 4 shows representative chronoamperograms of each molecular weight.

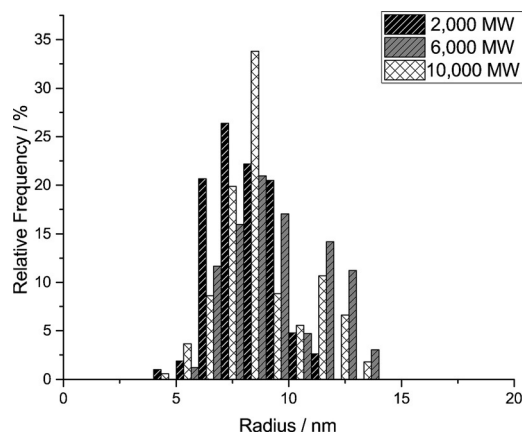


**Figure 4.** Representative chronoamperograms of silver nanoparticles capped with a) 2000 MW PEG, recorded at 1.7 V for 50 s, b) 6000 MW PEG recorded at 1.7 V for 300 s, and c) 10,000 MW PEG, recorded at 1.6 V for 600 s. Each inset is one highlighted feature from the given chronoamperogram.

### Electrochemical sizing

The spikes in the current observed in the chronoamperograms were integrated, and the charge converted to an equivalent radius (by applying Faraday's first law, and by assuming the particles to be spherical). The 2000 MW nanoparticles had

a mean radius of  $7.8 \pm 1.3$  nm (in which the uncertainty is taken from the standard deviation of radii), whilst the 6000 MW NPs are sized at  $7.9 \pm 3.3$  nm, and the 10,000 MW particles are  $8.78 \pm 4$  nm. This is in excellent agreement with previous SEM sizing of this batch of nanoparticles,<sup>[22]</sup> which provided a radius of  $8.5 \pm 3.5$  nm. Figure 5 shows the distribu-

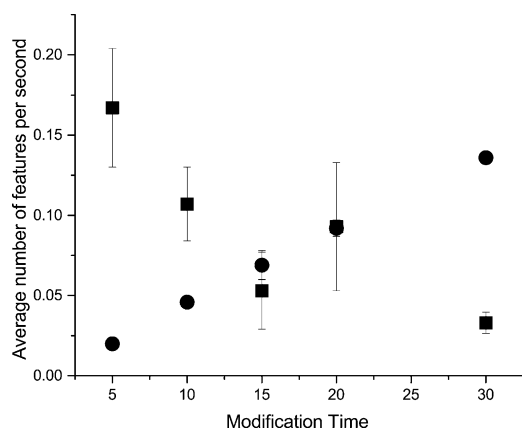


**Figure 5.** Sizing histogram displaying the relative frequencies of silver nanoparticles capped with 2000 ( $n = 112$ ), 6000, ( $n = 112$ ), and 10,000 MW PEG ( $n = 90$ ).

tion of sizes in each sample as measured electrochemically, which are in excellent agreement with one another and are over a small range of values. This indicates that the electrochemical sizing of the nanoparticles is not influenced by capping with variously weighted PEG, and that each spike corresponds to a single nanoparticle silver core undergoing full oxidation. However, the frequency of the impacts differed across samples of the same concentration of nanoparticles with different molecular weights. The implications of the variable frequency and the existence or absence of a time dependency is discussed next.

### Time dependency and frequency

To establish if the 2000 MW PEG NPs are accumulating at the electrode surface, and, therefore, could be said to demonstrate the same modification time dependency as previously observed<sup>[20]</sup> in the case of the 6000 MW PEG capped NPs, the time at open circuit potential between scans was systematically varied from five to 30 minutes. For consistency, this was also repeated using the 6000 MW PEG. The 10,000 MW PEG returned such a low frequency of impacts that the presence or absence of a time dependency is unclear. In contrast, Figure 6 shows the average number of spikes observed per second over three chronoamperograms recorded at 1.7 V with the stated modification time in place between scans. The 6000 MW PEG, as previously reported,<sup>[20]</sup> show a linear relationship between the number of features and the modification time, reflecting accumulation of material at the electrode surface. In contrast, the 2000 MW PEG displays a random distribution of the number of features per second with modification



**Figure 6.** Average number of impacts observed per second after a stated modification time at open circuit potential of 2000 MW PEG Ag NPs (square), and 6000 MW PEG (circle). Errors shown are Standard Error of the Mean.

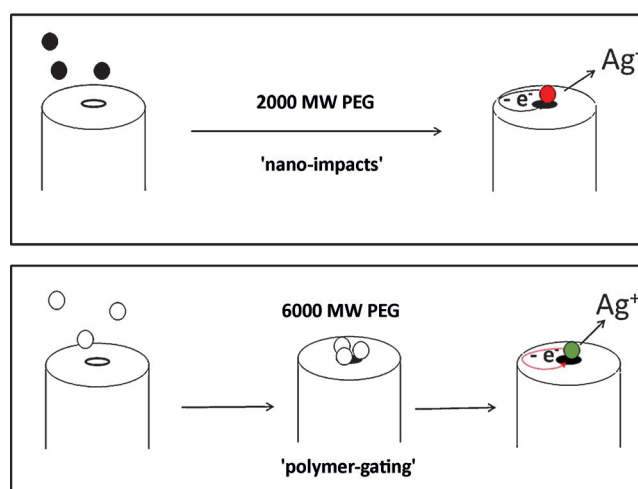
time, suggesting that there is no accumulation of the 2000 MW PEG NPs at the electrode. To establish the frequency of impacts, beginning with the 2000 MW NPs, the number of features observed per second of chronoamperogram was averaged across all scans. This gave a frequency of impacts of  $0.07 \text{ s}^{-1}$ . In the calculation of the frequency of both the 6000 MW and 10,000 MW PEG NPs, the modification time imposed was taken into account, returning frequencies of 0.02 and  $0.007 \text{ s}^{-1}$ , respectively. The increase in the Stokes radius of the nanoparticle will result in a smaller diffusion coefficient, and thus it is not inconsistent with the observed decrease in frequency with increasing molecular weight of the capping agent. However, the differing time dependencies of the 2000 and 6000 MW NPs suggests that the capping agent is differently implicated in its role in the electron-transfer process.

### Mechanism

The modification time dependency observed in the frequency of features of the 6000 MW PEG Ag NPs is consistent with a polymer-gating mechanism, as previously established for experiments using commercially prepared PEG NPs.<sup>[20]</sup> This mechanism involves an accumulation period, whereby nanoparticles diffuse to and arrive at the electrode. Once adsorbed on the electrode, the NPs then undergo a reversible partial “unwrapping” process, in which the polymer capping the nanoparticle partly uncoils. Once the large polymer has unwrapped sufficiently so it no longer prohibits electrical contact with the silver core, electron transfer can occur, resulting in an irreversible oxidation of the silver core to  $\text{Ag}^+$ . The key piece of evidence for this mechanism is the modification time dependency, which reflects accumulation of nanoparticles at the electrode surface, at which the number of oxidative features observed correlates to the length of time the electrode is submerged in the solution is held at open circuit potential, allowing the nanoparticles to “unwrap” at the electrode surface. Moreover, if the polymer did not inhibit the electrochemical process, then any pre-adsorbed nanoparticles should be oxidised within the first 10 s of milliseconds after application

of an anodic potential to the working electrode. As can be seen from Figure 4, the oxidative features corresponding to the NP oxidation are found to occur stochastically on a time-scale of seconds to minutes after the start of the chronoamperogram. The accumulation of the nanoparticles is critical to this mechanism, as this demonstrates the role of the capping agent in “gating” the electron-transfer process.

In the case of the 2000 MW nanoparticles, no such time dependency is observed. This suggests that in the case of NPs with lower weight capping agents, the PEG does not appreciably hinder electron transfer. This is supported by the DLS results, which show that the 2000 MW NPs are equivalently sized to the citrate-capped NPs, but smaller than the higher-weighted PEG NPs. The oxidation observed in this case is comparable to a “nano-impact” mechanism, previously observed in aqueous systems, for which the capping agent does not play a significant role in the oxidation.<sup>[15]</sup> This mechanism involves diffusion of the NP to the electrode (via Brownian motion), followed by the NP making contact with the electrode held at a sufficiently positive potential, and finally, oxidation of the NP to  $\text{Ag}^+$ . “Nano-impacts” are characterised by a random frequency of spikes at each modification time, as there is no pre-accumulation time.<sup>[12,21]</sup> This lack of nanoparticle accumulation is further evidenced by the absence of a stripping wave in a cyclic voltammogram after a waiting period of 15 minutes (Figure S1 in the Supporting Information). Figure 7 is a schematic illustrating the two proposed mechanisms. The



**Figure 7.** Schematic outlining the two proposed mechanisms of oxidation of silver nanoparticles to  $\text{Ag}^+$ , with the 2000 MW PEG oxidation progressing unhindered by the polymer (nano-impacts) and the 6000 MW PEG undergoing a polymer-gated oxidation.

10,000 MW PEG-capped nanoparticles experience such a low frequency of oxidation such that it is not possible to conclusively discern the operative electrochemical mechanism. However, it is clear that the very large capping agent component blocks electron transfer with the silver core, such that a large proportion of the nanoparticles are rendered electrochemically inactive. This, combined with the larger Stokes radius of the

molecule, results in a very low observed frequency. This differentiation provides evidence that the composition of the capping agent may be manipulated to control the mechanism by which the NPs undergo electron transfer, and corroborates the role of the capping agent in “gating” the reaction in the case of the higher-weight PEG capping agents.

## Conclusions

The manipulation of the capping agent characteristics, in this case, the molecular weight of poly(ethylene) glycol molecules, facilitates a controlled shift in the mechanism of electron transfer of nanoparticles in RTILs. It has been shown that the capping agent plays a large role in electron-transfer dynamics, and that the nanoparticles’ electrochemical behaviour can shift with relatively minor changes made to the capping agent.

To this end, it has been demonstrated that the frequency of nanoparticle oxidation is limited as the molecular weight of the PEG chains is increased, from  $0.07\text{ s}^{-1}$  for the 2000 MW NPs, to  $0.02$  and  $0.007\text{ s}^{-1}$  for the 6000 and 10,000 MW NPs, respectively, as is consistent with an increase in the Stokes radius, and a shift from “nano-impact” to “polymer-gating” mechanisms is observed moving from 2000 to 6000 MW PEG Ag NPs.

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**Keywords:** capping agents · ionic liquids · polymer-gating · nanoparticles · single nanoparticle impacts

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