Substrate mediated dissolution of redox active nanoparticles; electron transfer over long distances

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ABSTRACT

Reflective dark field microscopy is used to observe the decrease in the light scattered from Ag nanoparticles immobilised on differing solid substrates. The nanoparticles are exposed to solutions containing halide ions, both at open circuit and under potentiostatic control, leading to the loss of the nanomaterial. By coupling optical and electrochemical techniques the physical origin of this transformation is demonstrated to be the electrochemical dissolution of the metal nanoparticles driven by electron transfer to ultra-trace dissolved oxygen. The dissolution kinetics of the surface-supported metal nanoparticles is compared on four substrate materials (i.e., glass, indium titanium oxide, glassy carbon and platinum) with different electrical conductivity. The three conductive substrates catalyse the redox-driven dissolution of Ag nanoparticles with the electrons transferred from the nanoparticles, via the macroscopic electrode to the dioxygen electron acceptor.

KEYWORDS

substrate, electrocatalysis, oxidative dissolution, metal nanoparticles, optical microscopy, electrochemistry

1 Introduction

Probing the redox chemical behaviour of metal nanomaterials is critical to understanding their corrosion and dissolution. These chemical transformations have important implications for various scenarios including nano-toxicity in aquatic environments [1–3], electronics [4, 5] and cell [6–8] degradation. In particular, the chemical stability of the metal against oxidation is a key factor. The oxidation of metal nanoparticles often leads to the direct or ultimate production of dissolved metal species, where the resulting speciation depends on the identity of the used electrolyte and its concentration [9]. The dissolution process is therefore intimately associated with the nanoparticles' redox chemistry. Consequently, much work has focused on the study of the solution phase redox behaviour of NPs [10–13]. For instance, in the case of silver, the release kinetics of Ag⁺ from Ag nanoparticles has been studied to prove the size-dependent equilibrium of their oxidation based on the measurement of the equilibrated silver ion concentrations [12]. However, solution phase studies are often complicated by the need to use relatively high concentrations of nanoparticles and the dynamic process of their agglomeration in the presence of dissolved salts. The critical coagulation concentration of a monovalent electrolyte for Ag nanoparticles is some 10 mM and of divalent ions is 0.1–1 mM [13, 14] and such electrolyte concentrations routinely occur in real world environments. Consequently, decoupling information regarding the chemical transformation from the physical agglomeration/aggregation of the particles in solution can be challenging.

Despite problems in studying the process in the solution phase, electrochemistry remains an attractive candidate method for investigating nanoparticle redox behaviour using an electrode

to support the particles. For example, stripping voltammetry is commonly used to study the effects of particle apparent size [15], agglomeration [16], coverage [17] and assembly methods [18] on the nanoparticle oxidation. In this way, the influence of electrolyte [19] and the interactions of the metal NPs with the substrate electrode [20] or their attached surface functional groups have also been investigated [21]. Such electrochemical methods necessarily require the polarisation of the electrode to drive/control the particles' oxidation. However, we speculate that nanoparticle oxidation might also be driven by electroactive species in the solution (see Fig. 1) in a similar way to which metal corrosion occurs spontaneously under open circuit conditions especially in the presence of molecular oxygen. Under both conditions, no external currents flow with the oxidative dissolution flux matched by that of the oxygen reduction on a macroscopic conductive solid surface. However, typical corrosion of a bulk metal results from the electron transfer from itself to dissolved oxygen, destroying the macroscopic metal surface, whereas in the proposed nanoparticle oxidation the electron transfer is mediated by the supporting conductive substrate which suffers no change and is therefore catalytic. The aim of this paper is to validate this latter speculation.

Metallic nanoparticles are visible using a dark-field optical microscope within a wide size limit between ca. 10 and 100 nm in diameter [22, 23] and under suitable conditions individual particles or their clusters can be separately monitored [24]. This is in contrast to many other experimental techniques which are often limited to measuring the average response across a nanoparticle population. Optical microscopy can not only allow the position of each particle to be identified [25–29] but also enable changes in the chemical identity of solid particles to be monitored on the basis of the differences in their spectral

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Figure 1 Schematic of a redox-driven dissolution of metal nanoparticles by electron transfer over macroscopic distances. Molecular oxidising agents notably dissolved oxygen in trace amounts may oxidise the nanoparticles by electron transfer via a conductive substrate with charge injection from the latter at any point on the electrode surface.

properties [30–36]. Due to the ability to provide complementary information, recent work has focused on the coupling of optical and electrochemical techniques to facilitate the investigation of redox processes at the nanoscale [37–49].

In a typical electrochemical study of the redox behaviour of metal nanoparticles, the electrode is assumed to be neither chemically nor catalytically active in the studied conditions. Little attention has thus been paid to examining the potential influence of the substrate on the nanoparticles' redox behaviour. Recent work [21] has reported a clear dependence of the oxidation potential of Ag nanoparticles on the chemical nature of the underlying electrode material. Despite the lack of a well-understood origin of the observations, these results imply the possible influence of the substrate on the reaction mechanism of the redox processes. Moreover, it is important to note that even on the same conductive substrate surface, the interfacial potential difference at different locations can vary due to, for instance, the size-dependent surface energy of Ag nanoparticles [50] as in electrochemical Ostwald ripening [51] where larger particles grow at the expense of smaller particles through the electron transfer via the substrate. However, the role of the substrate has been largely overlooked in the numerous studies of nanoparticle chemistry but maybe in fact be decisively influential. As will be shown in this work the presence of a conductive substrate under commonly encountered conditions can catalyse nanoparticle dissolution. The effect is accentuated by the usually larger area of the substrate compared to that of the nanoparticles.

In the following we combine electrochemistry and optical microscopy to study the oxidative dissolution kinetics of supported silver nanoparticles under open circuit conditions, demonstrating a significant role of the substrate. We further discuss what comprises a “sufficiently good” electrical connection to facilitate the mediated dissolution.

2 Experimental

2.1 Chemicals

Citrate-capped nominally 100 nm-diameter spherical Ag nanoparticles were purchased from nanoComposix, USA (NanoXact, 0.02 mg·mL⁻¹ silver, 2 mM sodium citrate). The particle diameters have been characterised by transmission electron microscope (TEM) as 89 ± 12 nm (see Fig. S1 in the Electronic Supplementary Material (ESM) for further details). Potassium iodide, potassium bromide, chloride and potassium nitrate were purchased from Sigma-Aldrich and used as received (all ≥ 99.9%). Argon and oxygen gas cylinders were purchased

from British Oxygen Company, Surrey, UK. All solutions were prepared with deionised water (Millipore, USA) of an electrical resistivity of 18.2 MΩ·cm at 25 °C.

2.2 Optical microscopy

Optical measurements were conducted on a Zeiss Axio Examiner A1 microscope. The objective lense has a magnification of 10× with a numerical aperture of 0.3 (EC Plan-Neofluar, Carl Zeiss Ltd., Cambridge, UK). 2D black-and-white optical images were acquired by a Hamamatsu ORCA-Flash 4.0 Digital CMOS camera (Hamamatsu, Japan), giving 16-bit images with 4 megapixel resolution.

2.3 Optical measurements and data analysis

The optical measurements as a function of immersion times were done *ex situ* on a glassy carbon substrate surface. The surface of a GC electrode (*d* = 3.00 mm, electrical resistivity 50 μΩ·m, BASi, USA) was cleaned and mechanically smoothened by polishing on two microclothes loaded with very dilute alumina powder suspensions (0.2 g solid mixed with 5 mL DI water) of decreasing diameters of 0.3 and 0.05 μm. In addition, lens tissue was used to wipe off the residual alumina particles from the surface. Then the Ag nanoparticles were dropcast onto the cleaned substrate with a loading of 0.9 ± 0.1 μg·cm⁻² (or 2.4 × 10⁸ particles·cm⁻²) and dried under a nitrogen flow. The drop-cast area on the modified substrates was then visually focused using reflective dark field illumination (see Section 2 in the ESM) with an exposure time of 500 ms and the mean scattering light intensity of Ag nanoparticles was measured as the initial intensity value for *t* = 0 s. Subsequently, the same modified substrate was immersed in a 0.2 M KI solution for a time period of directly 6 min (or 50 min in the study of halide identity effects) at 25 °C, followed by rinsing with deionised water before drying to avoid the formation of salt microcrystals. The dried substrate was placed in the same position in the chamber for measuring the light intensity at *t* = 6 min (or 50 min).

For monitoring the dissolution kinetics of the silver particles in varying concentrations of iodide in Section 3.3, the same modified substrate was immersed in a 0.2 M KI solution for a time interval cumulatively to reach *t* = 5, 10, 30, 60, 120, 240, and 360 s, and the subsequent procedure described above was repeated until the cumulative immersion time reached the final 6 min.

For the study of the substrate influence in Section 3.4, three other different materials of glass, ITO and Pt were used as the substrates. The disc substrate of single crystal platinum (110) was fabricated by fastening at the thin end of a micropipette tip with an exposed 2.00 mm-diameter disc area. The cleaning of this Pt disc surface is the same as that of the GC, whereas the surfaces of the coverslip substrates, glass (22 mm × 22 mm, 0.13–0.17 mm thick, Sigma-Aldrich) and indium titanium oxide (25 mm × 25 mm, 1.1 mm thick, surface resistivity 8–12 Ω·square⁻¹, SPI, USA) were cleaned by washing with acetone and deionised water thoroughly. As such, after being modified with the Ag nanoparticles of the same loading, the substrate was immersed in 0.2 M KI or deionised water for 6 min at 25 °C. The scattered light intensity of the particles was measured before and after the immersion time.

Zen 2 Pro (Carl Zeiss Ltd., Cambridge, UK) was used for imaging processing and intensity analysis. The data was normalised to the initial value of *t* = 0 s and averaged over at least three repeat measurements for the plotted remaining fractions of the scattering light intensity.

2.4 Combined optical and electrochemical measurements

Potentiostating and cyclic voltammetry were performed using a μ -Autolab type II potentiostat (Eco-Chemie, Netherlands) with a three-electrode set-up in a home-built Faradaic cage. For studying the effects of potentiostating in Section 3.2, the GC electrode was used as the working electrode, and a platinum foil as the counter electrode and a leakless Ag/AgCl (3.4 M KCl) electrode as the reference electrode. A cleaned GC electrode was modified with Ag NPs of the same surface coverage as above. The modified electrode was inserted in air-saturated 0.2 M KI solutions and held at the fixed potential between -0.73 and $+0.25$ V vs. Ag/AgCl for 6 min. Last, the electrode surface was rinsed with deionised water and dried for the optical measurements of the dropcast nanoparticles. The cyclic voltammetry of the nanoparticle-modified electrode, the freshly modified electrode was polarised in an Ar-saturated 0.2 M KI solution in the potential range between -0.75 and $+0.25$ V (vs. Ag/AgCl) at a scan rate of $0.1 \text{ V}\cdot\text{s}^{-1}$.

For studying the effects of oxygen concentration, 0.2 M iodide solutions were purged with O_2 and argon thoroughly for 30 min. The air saturation was obtained by air equilibration with a freshly prepared iodide solution. Cathodic cyclic voltammetry of a clean macrodisc glassy carbon electrode was carried out in O_2 and air saturated solutions, and of a carbon microfibre electrode ($d = 7 \text{ }\mu\text{m}$ and $l = 1 \text{ mm}$) was conducted in an Ar-saturated solution at a scan rate of $0.05 \text{ V}\cdot\text{s}^{-1}$, to measure their oxygen concentration, respectively. Next, a GC electrode was modified with silver nanoparticles as described above and the same modified substrate surface was immersed in the freshly degassed 0.2 M KI in a rubber-sealed three-necked glass bottle for a time interval cumulatively to reach $t = 5, 10, 30, 60, 120, 240$ and 360 s. A gas atmosphere was constantly kept above the liquid surface with a very slow flow of the gas. During the intermission of the immersion of the modified electrode, once the electrode was taken out from the three-necked bottle a block of pressure-sensitive adhesive was used for the temporary sealing. The electrode rinsing and drying and optical measurements of the dropcast nanoparticles after each immersion were repeated until the cumulative immersion time reached the final 6 min.

3 Results and discussion

We first demonstrate how silver nanoparticles can be readily visualised on an opaque carbon support using reflective dark field microscopy. Optical measurements from the presented dark field images provide a quantitative route by which the surface supported nanoparticles population can be monitored. Exposure of the surface supported nanoparticles to a halide containing solution leads to their more rapid disappearance from the surface. This catalysed removal is evidenced to arise

due to the electrochemical dissolution of the nanomaterial driven by electron transfer through the substrate to trace dissolved dioxygen. Subsequently, the role and influence of the supporting substrate upon this dissolution process is evidenced.

3.1 Optical measurements of scattering from silver nanoparticles

Silver nanoparticles are plasmonic and both strongly scatter and adsorb light in the range of $400\text{--}500 \text{ nm}$. The surface plasmon resonance peak position depends on a number of factors including the particle size, shape and agglomeration state [14, 52]. Under dark field illumination individual silver nanoparticles as small as $10\text{--}15 \text{ nm}$ in diameter can be observed under optimal conditions [22, 23]. If the dimensions of the nanoparticle are below the wavelength of the light, on a microscope image a single nanoparticle appears as an individual diffraction-limited spot. This imaging technique can be used to visualise particles both in the solution and supported on a substrate [40, 41]. In this work, we drop-cast silver nanoparticles onto a glassy carbon macrodisc electrode ($d = 3.0 \text{ mm}$) and visualised the interface under dark field illumination (see Section 2 in the ESM for further details on the microscopy setup).

Figure 2(a) shows a representative microscope image of a glassy carbon surface dropcast with silver NPs (loading: $0.9 \pm 0.1 \text{ }\mu\text{g}\cdot\text{cm}^{-2}$, or $2.4 \pm 0.3 \times 10^8 \text{ particles}\cdot\text{cm}^{-2}$). Due to the distinctive “coffee ring” effect [53, 54] the edge of the dropcast area is clearly visible on the microscope image. At the corners of the image the glassy carbon appears black due to only minimal light scattering by the surface. In contrast the central area of the image is bright due to the presence of the nanoparticles. As can be seen in Fig. 2(a), the light intensity across the dropcast area is highly heterogeneous with brighter patches representing clusters of nanoparticles on the electrode surface (see Section 3 in the ESM for more details). Previous work has evidenced that drop-casting of nanoparticles leads to significant surface agglomeration of the material during the drying process [16]. Consequently, although the microscope image can yield information about the presence of the nanoparticles on the electrode surface, given the average inter-particle separation (estimated to be 560 nm for a uniform distribution) is comparable to or less than the wavelength of light, the microscope images cannot be used to provide detailed information regarding individual nanoparticles, but the images can be used to provide quantitative information regarding the overall nanoparticle population. The silver nanoparticle modified electrode was immersed into an iodide (0.2 M) solution for 6 min under open circuit conditions. After the immersion process the surface was reimaged and the resulting micrograph is shown in Fig. 2(b). A noticeable decrease in the light scattering intensity is observed. If the electrode is submerged into pure DI water containing no dissolved iodide then this large decrease in the light scattering intensity does not occur.

Figure 2 Optical microscopy images of the drop-cast AgNPs on a dried glassy carbon surface (a) before and (b) after the 6 min's immersion in a (non-degassed) 0.2 M KI solution under open circuit conditions. (c) Light scattering intensity measured at the 6 min relative to the initial value in the presence and absence of 0.2 M KI, respectively.

To quantify this change in the microscope image, the mean light scattering intensity was measured across the dropcast area and background corrected (see Section 2 in the ESM for details) to account for light scattered by the underlying carbon substrate. Prior to immersion of the electrode the mean light intensity is found to be reproducible with a 20% standard deviation (see Section 4 in the ESM). This variation in light intensity may at least in part result from a minor change from the particle surface coverage (11% calculated from the error of nanoparticle loading). This therefore indicates that the mean light intensity when averaged over a larger area is relatively insensitive to the specific surface morphology and agglomeration state of the nanoparticles on the interface and hence can be used to quantify changes in the nanoparticle population. After 6 min of immersion of the electrode, the modified electrode was subsequently rinsed in DI water before air drying and imaging of the interface. The remaining fraction of the scattered light intensity is therefore calculated as the ratio of light intensity measured before and after exposure to the solution.

Figure 2(c) depicts the ratio of the scattered light intensity before and after the electrode has been immersed into either DI water or a 0.2 M iodide solution. In the case where the electrode is exposed to de-ionised water for a period of 6 min. After the immersion process, the microscope image light intensity decreases by < 20%. This loss of light intensity is found to occur immediately upon immersion of the electrode into the DI water and most likely arises due to the desorption and physical removal of a small fraction of the drop-cast material from the electrode surface. Note the exposure of the electrode to the DI water also results in surface redistribution of the particles but longer immersion time or further washing of the interface in DI water does not lead to any further loss in the light scattering intensity (see Fig. S5 in the ESM). This further indicates the around 80% of the nanoparticle have a mechanically stable connection to the glassy carbon electrode surface.

In contrast to the case where the electrode is immersed into the DI water, immersion of the electrode into the 0.2 M iodide solution results in a major decrease in the light scattering intensity where only ca. 3% of the light scattering remains after this immersion process. This implies the near complete removal of Ag NPs from the electrode surface, which is confirmed by scanning electron microscopy imaging (see Section 6 in the ESM) of samples after immersion in water and in the iodide containing media. This observation is further evidenced in Section 3.3. The physical cause of this transformation is the focus of the following two sections.

3.2 Opto-electrochemical investigations of the redox processes

A silver nanoparticle modified electrode was submerged into an iodide containing solution. Upon immersion, the electrode was polarised with fixed potentials in the range of -0.75 to $+0.25$ V vs. Ag/AgCl. The mean scattering light intensity of the silver nanoparticles was measured before and after the 6 min immersion.

Figure 3 (black dots) plots the remaining fraction of the scattered light intensity as a function of the applied holding potential. Most notably, holding a potential below a threshold of ca. ~ -0.3 V (vs. Ag/AgCl) essentially completely inhibits the nanoparticle removal from the electrode surface, where approximately $71\% \pm 8\%$ of the light scattering intensity remains after exposure of the electrode. This value of $71\% \pm 8\%$ is consistent with that obtained when the electrode is immersed solely in DI water ($83\% \pm 16\%$). All the potentials above -0.3 V

Figure 3 The average remaining fractions of scattering intensity of the immobilised Ag particles on a GC electrode held at each different fixed potentials after 6 min' immersion in an air-saturated 0.2 M KI solution. The overlaid cyclic voltammograms of (solid) a freshly immersed, modified GC electrode and (dashed) a bare GC electrode in an Ar-saturated 0.2 M KI solution. Note that the vertical dashed line labels out the expected electrode potential for Ag/AgI under the condition. Scan rate $0.1 \text{ V} \cdot \text{s}^{-1}$.

lead to a quantitatively similar (within experimental error) loss of nanoparticles from the electrode surface.

The observation that the nanoparticle dissolution can be inhibited by the application of a potential to the underlying substrate provides strong evidence that immersion of the nanoparticles into the iodide solution leads to the loss of the nanoparticles via the occurrence of a redox reaction. Further Section 7 in the ESM demonstrates how the required threshold potential to avoid nanoparticle dissolution is sensitive to the ionic composition of the solution. For comparison in Fig. 3, overlaid with the optical data is a voltammogram of a drop-cast silver nanoparticle modified electrode measured in a solution containing 0.2 M potassium iodide. On the forward sweep of the voltammogram a clear stripping peak is observed at -0.22 V, corresponding to the oxidation of the surface adhered silver to silver iodide. On the reverse scan a corresponding reduction wave is observed at -0.45 V. In the presence of 0.2 M iodide the Ag/AgI redox couple has a reduction potential of -0.33 V, this potential is marked on Fig. 3 and is in good agreement with both the position of the voltammetric peaks and the threshold potential at which the iodide driven dissolution of the nanoparticles is inhibited.

Consequently, we infer that the dissolution of the silver nanoparticles from the modified electrode following immersion into the solution involves the oxidation of the silver

where the chemical products are either silver cations or silver salts (as discussed in Section 3.3). In addition, the evolution of the open circuit potential of the NP-modified electrode over the 6-min of immersion in the iodide solution shows a conspicuous change only in the first 60 s (Section 8 in the ESM). This period of time is similar to that for the major decrease (ca. 90%) in the light scattering intensity of the silver particles. This observation likely supports the occurrence of the electrochemical redox process.

Accepting that the nanoparticle loss originates from the oxidation of the nanoparticles, it is important to consider the identity of the counter reaction for which an obvious candidate oxidant is atmospheric oxygen. To investigate possible effects of dissolved dioxygen on the nanoparticle dissolution process, we prepared the iodide (0.2 M) solutions with different concentrations of oxygen corresponding to O_2 , air or Ar gas saturation conditions by purging each pure gas (except air) thoroughly for 30 min to the solutions in a well-sealed three-necked bottle.

For measuring the concentration of dissolved dioxygen in these degassed solutions, a glassy carbon macrodisc electrode ($d = 3.00$ mm) was inserted into the O_2 and air-saturated solutions and was then scanned voltammetrically using applied potentials from -0.1 to -1.0 V vs. Ag/AgCl, whilst a carbon microfibre electrode ($d = 7$ μ m and $l = 1$ mm) was preferred under argon saturation so as to probe the ultra-low concentrations encountered [55], leading to currents of the order of nA recorded by scanning a potential range from -0.1 to -1.5 V after immersion in the solution.

Figure 4(a) shows an irreversible reduction peak at -0.7 V for both O_2 and air saturated solutions, which is due to the two-electron reduction of O_2 to H_2O_2 under the neutral condition [56]. The peak currents for oxygen and air saturation conditions are measured to be 30.4 ± 3.4 and 8.6 ± 0.7 μ A, respectively. Using the Randles–Ševčík equation for irreversible peak currents [57], the reduction currents correspond to 1.20 ± 0.1 and 0.31 ± 0.02 mM of dissolved O_2 in the respective bulk solutions (see Section 9 in the ESM for detail calculations and for those below regarding the oxygen concentration), which are consistent with the literature [56]. In the case of argon saturation, the microelectrode voltammogram as seen in the inset of Fig. 4(a) shows a tiny quasi-steady-state current of oxygen reduction in the potential range between -1.0 and -1.2 V, where no significant solvent breakdown is observed. Using linear extrapolation from the capacitive current at potentials

above -0.5 V, the quasi-steady-state current is background subtracted and measured to be 1.2 ± 0.7 nA. This is then calculated to correspond to an oxygen level of 1.2 ± 0.7 μ M. An aging time of 6 min still retains a reduction current of 2.3 ± 0.4 nA and thus an O_2 concentration of 2.3 ± 0.4 μ M, indicating a desired air tightness of the vessel.

For the subsequent optical measurements, a GC surface modified with Ag nanoparticles was immersed in the three KI solutions each containing one of the different levels of dissolved dioxygen described above. Control experiments in the deionised water with the O_2 , air and Ar saturation, respectively, were also done. The scattering light intensity of the particles was monitored as a function of time at each oxygen concentration of 1.2 mM, 0.3 mM, and 1–2 μ M. In the absence of iodide, the light intensity is generally essentially constant although in few cases including some of the experiments in Fig. 4(b) there is a ca. 5%–10% variation in the measured light intensity. The figure shows that in the presence of iodide, despite the greatly lowered O_2 concentration to few micromolar there is no marked influence on the dissolution process. Although one may anticipate that the removal of oxygen might inhibit the reaction, the complete removal of oxygen from the solution by gas purging is not feasible. Indeed in this work the use of denser inert gas of argon than dinitrogen and an airtight container has enabled to reach a significantly low level of dissolved oxygen, 1–2 μ M. This level of dissolved oxygen is further improved compared to that reported in the literature (7–14 μ M using N_2 outgassing) [55, 58]. Nevertheless despite the inconclusive result for dissolved oxygen, we note that other candidate oxidising agents, notably protons or triiodide ions (which may form upon the aging of iodide solutions), are excluded on the basis of the results presented in Section 10 in the ESM. Therefore, we believe that the only likely oxidising agent is the trace oxygen. First, the trace amount of O_2 at μ M levels is considered to be sufficient for the reaction given the tiny mass of silver (0.1 nmol) to be oxidised. Second, micromolar levels of oxygen would be insignificant in many reactions but in the present case the oxygen only needs to be present in the diffuse layer at any point of the conductive electrode surface to be effective (see Section 3.4). Even oxygen molecules which are close to the electrode but remote from the particles by some millimetres can oxidise them via the conductive substrate mediating the electron transfer as in classical models of corrosion, and as explored and discussed further below. Hence, the influence of oxygen is much amplified because of the possibility of the oxidising agent acting remotely. Consequently, the lack of sensitivity of the silver nanoparticle dissolution to the “removal” of oxygen most likely reflects the fact that the oxygen reduction process is, in this case, not the rate determining step.

3.3 Optical study of the Ag nanoparticle dissolution process

The above results provide evidence that the nanoparticle loss involves the oxidation of the nanoparticles in accordance with Eq. (1). Given halide ions have a strong affinity towards argentous ions, the rate of this dissolution process is likely sensitive to both the halide identity and concentration. To investigate this experimentally, silver nanoparticle modified electrodes were immersed for a period of 50 min into differing halide containing solutions (KI, KBr and KCl) and also into a solution containing 0.2 M KNO_3 under open circuit conditions. In a further experiment, the concentration of the iodide was varied from 0.2 to 0 M and the silver nanoparticle light scattering intensity was monitored as a function of time at each concentration.

Figure 4 (a) Voltammetric responses of the reduction of dissolved dioxygen using a glassy carbon macrodisc electrode ($d = 3.00$ mm) immersed in (red) oxygen-saturated and (black) air-saturated 0.2 M KI solutions and using a carbon microfibre electrode ($d = 7$ μ m and $l = 1$ mm) in (green) an argon-saturated solution. The inset presents the enlarged version of the green curve for zero aging time while the purple curve denotes the voltammogram after an aging time of 6 min. Scan rate 0.05 V·s⁻¹. (b) Light scattering intensity relative to the initial value as a function of time (within 6 min' total immersion time: 0, 5, 10, 30, 60, 120, 240, and 360 s) measured in (hollow spots) non-iodide containing solutions and (solid spots) 0.2 M KI solutions with varying concentrations of dissolved oxygen: (green) 1–2 μ M with Ar saturation, (black) 0.3 mM with air saturation and (red), 1.2 mM with O_2 saturation.

Figure 5(a) demonstrates that in the nitrate containing solution, the scattered light intensity after exposure is essentially unaltered from that found with DI water. However in the other solutions, a significant reduction of intensity is observed in the order $KI < KBr < KCl < KNO_3$. This ordering directly relates to high halide-containing media (0.2 M) where the soluble $Ag(I)$ halide complexes, $AgX_n^{(n-1)-}$ are formed via the reaction

where ($X = I, Br$ or Cl , and $2 \leq n \leq 4$) and for which

$$K(AgX_n^{(n-1)-}) = \frac{[AgX_n^{(n-1)-}]}{[Ag^+][X^-]^n} \quad (3)$$

where, for instance when $n = 2$, $\log[K(AgX_2^{(2-)-})] = 11.5$ ($X = I$) > 7.5 ($X = Br$) > 5.2 ($X = Cl$) at $25^\circ C$ [59] as discussed below. The same trend is also found for the soluble higher silver halide complexes [59]. This sensitivity to the halide ion is also reflected in the kinetic data shown in Fig. 5(b) where the rate at which the nanoparticle dissolution occurs is shown to be sensitive to the iodide concentration.

The observed halide effects strongly suggest that the final products of the silver oxidation in the iodide solutions are iodide compounds of silver(I). We infer that either, despite the volume expansion, the solid particles of silver monoiodide scatter less light than metallic silver or, alternatively, that further soluble silver iodide complexes account for the observed scattering loss by dissolution of the particles leading to their

reduction in size. We experimentally exclude the possibility of $AgI(s)$ formation due to both observations of very few particles seen by SEM (Section 6 in the ESM) and no voltammetric fingerprint of this solid (see Section 11 in the ESM) on the NP-modified glassy carbon surfaces after 6 min' immersion in 0.2 M KI. Soluble silver iodide complexes are $AgI_n^{-(n-1)}$ where the integer $n \leq 4$ and have increasing cumulative formation constants with $\log[K(AgI_n^{-(n-1)})]$ of $6.6 < 10.7 < 13.4 < 14.1$ from $n = 1$ to $n = 4$ at $25^\circ C$ [59]. It can be calculated that all the AgI formed from the dropcast nanoparticles would, under thermodynamic control, dissolve to form the soluble complexes given the magnitude of the formation constants of the latter. Consequently, it is inferred that the oxidised silver in the iodide solutions is most likely dissolved into soluble silver iodide complexes via

3.4 Influence of the substrate on the dissolution kinetics

Having verified that the loss of the surface supported nanoparticles is due to their oxidative dissolution and demonstrated how this reaction can be controlled by the application of a potential to the substrate or changing the halide concentration and/or identity, we next turn to consider the possible influence of the substrate upon this dissolution reaction under open-circuit conditions. Silver nanoparticles were drop-cast onto four different substrate materials: platinum, glassy carbon, indium-tin oxide (ITO) and glass. These four substrates have markedly different conductivities. The surface mounted nanoparticles were subsequently exposed to either deionised water or a solution containing 0.2 M KI for a period of 6 min. As done previously the light scattering intensity was measured prior to and after exposure of the material to the solution.

Figure 6 plots the scattered light normalised to its initial value for the four substrates, with and without the presence of the halide ions. In the absence of halide, the remaining fraction of the scattered light intensity varies with the substrate identity $-63\% \pm 5\%$ for glass, $75\% \pm 5\%$ for ITO, $83\% \pm 16\%$ for glassy carbon and $92\% \pm 11\%$ for platinum. This relatively smaller variation in the fraction of the remaining scattered light intensity where the nanoparticles have been exposed to DI water most likely reflects the different adhesion strengths of the nanoparticles to the substrate materials [60]. However, adhesion strength cannot solely explain the comparative rates of loss in the presence of iodide which varies markedly across the different substrates. For the glass supported nanoparticles, immersion

Figure 5 (a) Optical measurements of the remaining fraction of the total scattering of drop-cast Ag NPs on a glassy carbon electrode surface at open circuit potentials after 50 min' immersion in 0.2 M halide, KNO_3 solutions; the solid line denotes that measured in deionised water, along with the dashed lines represent the upper and lower limits from the standard deviation. (b) Light scattering intensity relative to the initial value as a function of time (within 6 min' total immersion time: 0, 5, 10, 30, 60, 120, 240, and 360 s) measured in KI solutions with varying concentrations of (grey) 0 M, (orange) 0.05 M, (green) 0.1 M and (navy) 0.2 M.

Figure 6 Optical measurements of the remaining fractions of Ag scattering, after 6 min' immersion in (white) deionised water or (black) 0.2 M KI solutions under the open circuit condition, as a function of differently conducting substrates. The green data present the specific values of the substrate conductivity.

into a solution containing iodide reduces the nanoparticle scattering light intensity by only a further $7\% \pm 5\%$ such that after immersion $56\% \pm 3\%$ of the scattering light intensity remained. This is in stark contrast to the platinum and carbon substrates where exposure to the iodide solution decreases the scattering light intensity by a further $78\% \pm 16\%$ and $81\% \pm 13\%$ respectively. The ITO substrate is found to show a response in between these two limits where exposure of the nanoparticles to the iodide solution leads to a further $41\% \pm 5\%$ decrease in the light scattering intensity. It is of importance to note that in the case of the glass substrate, the substitution of the glass does not completely inhibit the iodide driven dissolution mechanism. For the nanoparticles supported on a glass substrate, when they are exposed to the iodide solution for longer periods of time ca. 1.5 h (see Section 12 in the ESM) the nanoparticles are found to be completely removed from the surface, this removal does not occur in the absence of the iodide. This result evidences that the oxidative dissolution reaction proceeds even without the presence of a conductive substrate, albeit rather slowly, but the presence of the electrode significantly increases the dissolution rate. The results presented in Fig. 6 are consistent with the idea that the substrate can significantly influence the rate at which the nanoparticle oxidative dissolution occurs. Given that the nanoparticle loss has already been demonstrated above to be an electrochemical process that can be directly controlled if a potential is held on the supporting substrate, it is reasonable to consider that the nature of the electrode support can influence the dissolution kinetics via two factors: the conductivity of the supporting material and the quality of the electrical connectivity of the particle to the surface. Overlaid on Fig. 6 is the variation in the conductivity of the materials used. At one limit glass is a near ideal insulator, ITO and glassy carbon have higher conductivities whilst platinum has the highest high conductivity, where the influence of the substrate material is found to be clearly correlated to its inherent conductivity. More precisely, we infer that the major effects of the substrate are to provide a threshold conductivity for either the dissolution via electron transfers within the electrode or not. Glass does not have sufficient conductivities whereas the others do, such that the “switch-on” of the substrate-mediated oxidative dissolution is observed as the substrate becomes more conductive. However, the conductivity differences between ITO, glassy carbon and platinum are so much that they cannot all be close to the threshold value. As such, the differences between the rates of the reaction observed on these electrode supports must also reflect differing NP/substrate contact resistances.

The increased nanoparticle dissolution that occurs on the conductive substrates (ITO, GC and Pt) indicates that electron transfer through the substrate is likely an important mechanism for the loss of the nanomaterial. Figure 7 presents a schematic for the proposed overall mechanism of the oxidative dissolution under open circuit conditions. Specifically it is envisaged that on a conductive supporting substrate the counter reaction—in this case likely oxygen reduction—occurs not at the nanoparticle but remote from it. Consequently, it is concluded that by providing an additional large area interface, much greater than the total surface area of all the nanoparticles (see Section 13 in the ESM for detailed calculations), at which the oxygen reduction reaction is able to occur, the substrate is able to essentially catalyse the nanoparticle oxidative dissolution!

Finally, it is of interest to reflect on previous work [61–63] which has shown that for nanomaterial that has been drop-cast onto an electrode surface, when the particles are studied voltammetrically either by stripping voltammetry [61, 62] or

Figure 7 Proposed mechanism for the electrochemical oxidative dissolution of Ag NPs under the open circuit condition, and the concept of a “voltage divider” for viewing the NP/substrate electrical contact. “ORR” stands for “oxygen reduction reaction”. E_{sol} , E_{NP} and E_{subs} are the electrical potential at the solution phase, the nanoparticle, and the local point of substrate respectively, whilst $R_{sol/NP}$ and R_c are the solution/nanoparticle interfacial resistance and the nanoparticle/substrate contact resistance respectively.

by investigating metal deposition on to the nanomaterial [63] it has been concluded that in many cases only a small fraction of the nanoparticle sample is in “good” electrical contact with the electrode surface [64]. Conversely, in the present results the presence of a conductive substrate has a marked effect on a very large proportion of the nanoparticles. Importantly, the application of a cathodic potential can, as shown in Fig. 3, completely inhibit the dissolution process, thus indicating that a very high fraction of the nanoparticles are in fact in electrical contact with the substrate. At first sight these two results are contradictory. However, it is illuminating to consider the timescales involved for each process, a voltammetric experiment is often run over the course of a few seconds, whilst conversely the present dissolution experiments span a time frame of minutes to hours. As schematically highlighted in Fig. 7, a voltage divider [65] can be a useful analogy for viewing the electrical contact of a surface supported nanoparticle with the substrate electrode where a redox reaction occurs at the nanoparticle interface and the electrons are provided through the supporting substrate. From this we can recognise that even if a nanoparticle has an ohmic contact with an electrode, the potential held on the nanoparticle is not necessarily the same as that of the electrode and will depend upon both the reaction occurring at the nanoparticle/solution interface and the contact resistance between the particle and the electrode. A relatively resistive contact between the nanoparticle and the electrode may not be sufficient to drive a reaction to occur on the timescale of seconds but may be sufficient, as is the case in the present work, to allow a reaction to occur over a longer timescales of minutes to hours. As such, what constitutes a “good” electrical contact depends upon the experimental timeframe.

4 Conclusions

Under reflective dark field illumination the scattered light from silver nanoparticles immobilised on a glassy carbon substrate is found to reduce over time under open-circuit conditions in a halide-containing solution (X^- , $X = I, Br, Cl$). By coupling the electrochemical actuation and optical monitoring, we demonstrate that the scattering decrease arises from a redox-driven dissolution of the metal nanoparticles into soluble halide complexes by electron transfer to trace dissolved dioxygen. Further, the comparison of the dissolution kinetics of the

surface-supported Ag nanoparticles on four differently conducting materials—glass, ITO, GC, and Pt—reveals that the presence of a conductive substrate is able to catalyse the oxidative dissolution. On this basis, the assessment of particle/electrode electrical connectivity is critically discussed with recent relevant studies and suggested to rely on the experimental timeframe.

Electronic Supplementary Material: Supplementary material (electron microscopy images of the silver nanoparticles, dark field microscopy set-up, complementary optical measurements of dropcast silver nanoparticles on the various substrates, open circuit potential measurements, and discussions and calculations regarding the oxidising agent) is available in the online version of this article at <https://doi.org/10.1007/s12274-021-3497-6>.

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