Collisional electrochemistry of laser-ablated gold nanoparticles by electrocatalytic oxidation of glucose

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Abstract

We report the electrochemistry of gold nanoparticles (AuNPs), prepared by Laser Ablation Synthesis in Solution (LASiS), via the electrocatalytic oxidation of glucose upon single nanoparticle collisions at inert microelectrodes. Spherical AuNPs with diameters in the range 20-30 nm, as determined by transmission electron microscopy, were synthesized by LASiS of a gold plate immersed in water. Nanoparticle collisions were electrochemically detected through the AuNP-catalysed oxidation of glucose at carbon fiber microelectrodes in alkaline solution, enabling the electrocatalytic detection of single AuNPs. This approach provides a basis for detecting and understanding the electrocatalytic properties of pristine nanoparticles in aqueous solutions.

Keywords: gold nanoparticles; laser ablation; glucose; electrocatalysis; nano-impact

1. Introduction

The diverse exploration and applications of nanoparticles has resulted in a significant increase in nanoparticle-based products, ranging from home disinfectants to industrial catalysts[1]. With the concomitant potential for increased release of nanoparticles into the environment, which pose potential risks to human health, it is highly desirable to develop effective analytical tools for the detection and characterization of single nanoparticles, particularly in complex aqueous systems[2]. In recent years, the innovative nano-impact electrochemical method, which is used to study *in situ* the behaviors of single nanoparticles in a liquid phase by virtue of their random collisions with electrode surfaces, has attracted considerable interest[3-5]. This method enables new insight into physical and chemical properties of solution-phase nanoparticles, such as size, concentration, presence of surface functionality, etc., which are complementary to conventional microscopic and

spectroscopic techniques such as transmission electron microscopy (TEM) and dynamic light scattering (DLS). For example, Sokolov et al.[6] applied the electrochemical nano-impact method to characterize Ag nanoparticles in solution, which allowed the nanoparticles to be classified according to irreversible aggregation and reversible agglomeration. Chen et al.[7] investigated the interactions between individual Au nanoparticles (AuNPs) and electrode surfaces modified with different terminal groups by analysis of electrochemical nanoparticle collisions, leading to a new approach to probe surface chemistry at the nanoscale.

Since the introduction of the electrochemical nano-impact method, many electrocatalytic reactions have been explored on various nanoparticles; e.g. Au[8], Pt[9], TiO_2[3] and IrO_2[10] have been extensively investigated to better understand electrocatalytic reaction mechanisms [11, 12]. Recently, AuNP suspensions were reported for the ensemble electrocatalytic oxidation of glucose at rotating disc electrodes[13]. In these reports, the nanoparticles are generally prepared by chemical approaches, which inevitably involve nanoparticle surface modification. Nanoparticle preparation by laser ablation synthesis in solution (LASiS)[14, 15] offers scope for preparation without recourse to chemical reagents. In this work, we introduce nano-impact electrochemistry at pristine AuNPs obtained by LASiS and employing electrocatalytic glucose oxidation[16] as the indicator reaction. The effect of applied potential on AuNP collisions at carbon fiber microelectrodes was also examined.

2. Experimental

2.1. Chemicals and materials

NaOH and α-D-Glucose were obtained from Sigma-Aldrich. Milli-Q water was used to prepare all aqueous solutions. AuNPs were prepared by LASiS, as previously described[14, 15]. Briefly, a thin gold disc (99.99 %) was ablated by placing the disc on the base of a glass vessel containing 10 mL of pure water (Lab PURE Plus UV system). The immersed metal plate was irradiated with the fundamental output (1064 nm) of a Nd:YAG laser (Continuum Surelite II) which was focused by a plano-convex lens with a focal length of 250 mm. The laser operated at a repetition rate of 10 Hz with a pulse width of 7 ns (fwhm) and a beam diameter (before focusing) of 8 mm. The laser was operated at a power of ~7.5 mJ $pulse^{-1}$, yielding an approximate ablation fluence of 2 x 10^5 mJ cm^{-2} $pulse^{-1}$. AuNP samples studied here were prepared by 60 min ablation in all cases.

2.2. Instrumentation & methods

Electrochemical experiments were performed with an Autolab PGSTAT 302N + ECD module at 100 pA current setting (Metrohm, The Netherlands) in a three-electrode cell composed of a platinum wire auxiliary electrode, a Ag/AgCl (3M KCl) reference electrode and carbon fiber (33 µm diameter) working electrode. The electrolyte solutions were saturated

with nitrogen during all electrochemical experiments. No attempt was made to overcome any instrumentation limitations, such as rise time, in the data presented here[7, 17]. The ECD module was used at the 100 pA setting and electrical cables TEM was conducted on a JEOL 2100 TEM operated at 200 kV. UV-visible absorption spectra were recorded on a GBC UV/Vis 916UV-vis spectrometer. AuNP samples for TEM were prepared by casting a drop of freshly-ablated AuNP suspension (0.6 nM) on a carbon-coated copper grid. AuNP-modified carbon fibre microelectrodes were prepared by drop-casting 5 μL of 0.6 nM AuNP suspension in water onto the microelectrode surface and allowing the water to evaporate. The surface plasmon resonance (SPR) band intensity, in combination with the TEM radius, was used to calculate the concentration of AuNPs in the suspensions, as previously reported[18]. For AuNP nano-impact experiments, 5 mL of 0.1 M NaOH was spiked with glucose solution and/or AuNP suspension to the concentrations indicated in the figure legends.

3. Results and discussion

Following LASiS, the AuNPs were characterized by UV-Vis absorption spectrophotometry and TEM. A strong absorption around 520 nm (Fig. 1A) was observed which is consistent with the well-established SPR adsorption band, expected in the presence of AuNPs. Fig. 1B shows a typical TEM image of the AuNPs, indicating that the majority of the particles were spherical. The diameters of at least 200 particles from each LASiS batch were obtained from the TEM images to characterize their size distribution. Fig. 1C shows a histogram of the nanoparticle diameters, suggesting a broad size distribution with an average particle diameter of 28 nm (standard deviation: 9 nm).

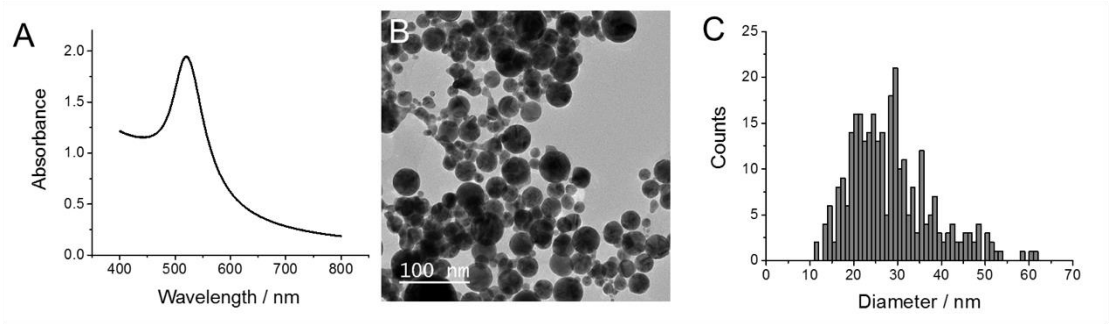

Fig. 1. (A) UV/Vis spectrum, (B) TEM image and (C) size distribution of the LASiS AuNPs.

The electrochemical behaviour of the LASiS-produced AuNPs towards glucose oxidation was investigated by cyclic voltammetry (CV). Fig. 2A compares the CVs of the carbon fiber microelectrode before (curve a) and after (curve b) modification by a layer of AuNPs by drop-coating. At the bare microelectrode, there was no current response to glucose due to the inertness of the carbon surface for this reaction in the potential region of interest (Fig 2A, curve a). However, a significant increase of the anodic current was observed at the AuNP-modified microelectrode, demonstrating the

electrocatalytic activity of the nanoparticles towards glucose oxidation (Fig 2A, curve b). In the positive-direction scan, the peak current at -0.25 V is attributed to oxidative transformation of glucose to gluconolactone at the surface of the AuNPs[19]. The second peak, in the potential range from -0.1 V to 0.4 V, is associated with successive oxidation processes that are highly-dependent on the formation of AuOH active species on the electrode[20], in this case the AuNP surface. A further increase of the potential resulted in the generation of Au oxide, which hindered glucose oxidation[20]. During the reverse scan, glucose is electrocatalytically oxidised again following the reduction of the inert Au oxide layer. The increased current on the reverse scan indicates that the reduction of the Au oxide, on the AuNP surfaces, produces a more active surface for glucose oxidation.

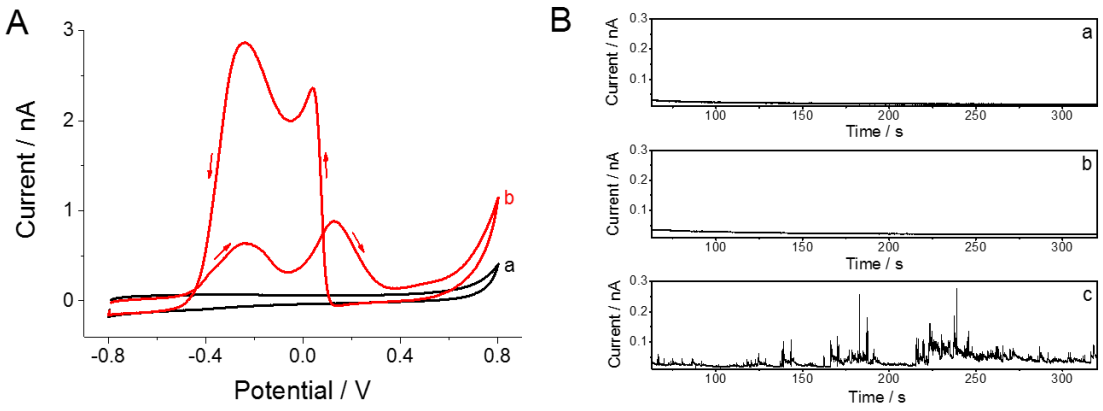

Fig. 2. (A) Cyclic voltammograms recorded in N_2-saturated 0.1 M NaOH containing 5 mM glucose at a carbon fiber microelectrode before (a) and after (b) modification with LASiS-produced AuNPs. Scan rate: 50 mV/s. (B) Chronoamperometric curves recorded at a carbon fiber microelectrode in N_2-saturated 0.1 M NaOH containing 5 mM glucose (a), 0.1 nM Au nanoparticles (b) and 5 mM glucose + 0.1 nM Au nanoparticles (c). Applied potential: 0.4 V.

The electrochemical nano-impact method was investigated with suspensions of AuNPs in solution. Fig. 2B compares the chronoamperometic curves obtained at 0.4 V in different solutions. As compared with the chronoamperometric curves obtained in either glucose (Fig. 2B, curve a) or AuNP (Fig. 2B, curve b) alkaline media, current spikes only emerged in the presence of both glucose and AuNPs (Fig. 2B, curve c), which suggests that the signals were produced from the electrocatalytic oxidation of glucose during AuNP collisions with the carbon electrode. The results indicate that the electrochemical nano-impact method is promising for detecting LASiS-produced nanoparticles as well as probing more complex electrochemical reactions when compared to the previously reported reactions for this technique such as hydrazine oxidation, hydrogen peroxide reduction and hydrogen evolution. The magnitude of the current spikes can be compared to values for diffusion-controlled reactions at a single nanosphere electrode sitting on a flat surface[17, 21, 22] according to the expression

$$I_d = 4\pi(ln2)nFDrc$$

where I_d is the diffusion-limited current, n is the number of electrons transferred per molecule, F is Faraday's constant, D is the diffusion coefficient, r is the spherical radius and c is the solute concentration. Taking values of n = 2, D = 6.7 x 10^{-6} cm^2 s^{-1}[20] and r = 14 nm, the limiting current is *ca*. 0.078(±0.025) nA (the precision estimate is based on the standard deviation of the AuNP diameter). This is in reasonable agreement with the experimental observations, but it must be noted that the glucose oxidation reaction is not necessarily diffusion controlled [20, 23] and that values of n can vary from 2 to 16[24].

Fig. 3 shows the effect of the applied potential on the current responses to the nanoparticle collisions. The magnitude and frequency of the spikes was enhanced with increasing applied potentials in the range from -0.2 V to 0.4 V, indicating the sensitivity of the nano-impact method for detection of the AuNPs on the electrochemical process of glucose oxidation (Fig. 3); i.e., as potential increases, the frequency and intensity increases. This indicates a more active electrochemical surface for glucose oxidation but may also offer additional mechanistic information regarding glucose oxidation on gold nanoparticles.

The overlayed bar charts in Fig. 3 show the distributions of spike transient magnitude with respect to applied potential. The spike transients were summarized by counting spikes in the first time derivative of the raw transient data, in-line with methods reported previously[22]. The spike magnitude and number of spikes detected with current magnitude greater than 2 pA increased at higher applied potentials. From the CV presented in Fig. 2A, oxidation of the gluconolactone intermediate occurs at potentials above -0.1 V. Therefore, the current observed at higher potentials, namely 0.0, 0.2 and 0.4 V, represents the current response at increasing over-potentials. The apparent increase in peak magnitude with applied potential is in agreement with the current-potential curve presented in Fig. 2A. Significantly, the frequency and magnitude of spikes increased and the spike shape changed with the applied potential. The increase in frequency with potential is interesting because the transport of NPs to the electrode surface is described by 'random walk' transport resulting from Brownian motion. While the stochastic nature of nanoparticle-electrode collisions has been thoroughly investigated[4, 25], the effect of electrode potential on impact frequency remains unclear. Previous work has discussed the importance of surface charge and the electric double layer in determining the nanoparticle-electrode interactions, specifically relating to charged capping agents such as citrate [7]. The pristine Au nanoparticles employed here exhibit an inherent negative surface charge which may be significant in determining the relationship between collision frequency and electrode potential. Surface charge effects were found previously to be influential on the morphology of electrodeposited metals on glassy carbon surfaces when metal nanoparticles were present in the plating solution[26]. It may also reflect the kinetics of electron transfer for this complex reaction, where the adsorption of intermediate species is followed by electron transfer, as well as the formation of gold oxides on the surface, all of which are sensitive to the applied potential[20, 23, 24]. This is also reflected in the data in Fig. 3 where a broad Gaussian distribution in the current magnitude is not seen but is skewed to collisions

with lower current magnitude. This is contrary to the work of Bard and co-workers who used the hydrazine oxidation reaction to measure the size distribution of nanoparticles where the magnitude and distribution of the current spikes correlated with the size distribution determined by TEM[22]. Therefore the oxidation of glucose under these conditions may be affected by the size and residency time of the nanoparticle, as well as adsorption and diffusion[27], and needs further investigation. The change in the spike shape with potential is also interesting and may be indicative of AuNP – carbon surface interactions. For example, in Fig.3C, the peak shapes indicate that particles stick to the surface and then undergo a slow desorption (or a fouling of the surface by glucose oxidation products). However the spikes in Fig.3A are sharper, indicative of particles that collide and move away quickly from the surface (or, again, a fouling of the AuNP by glucose oxidation products or formation of Au oxide[28] on the surface).

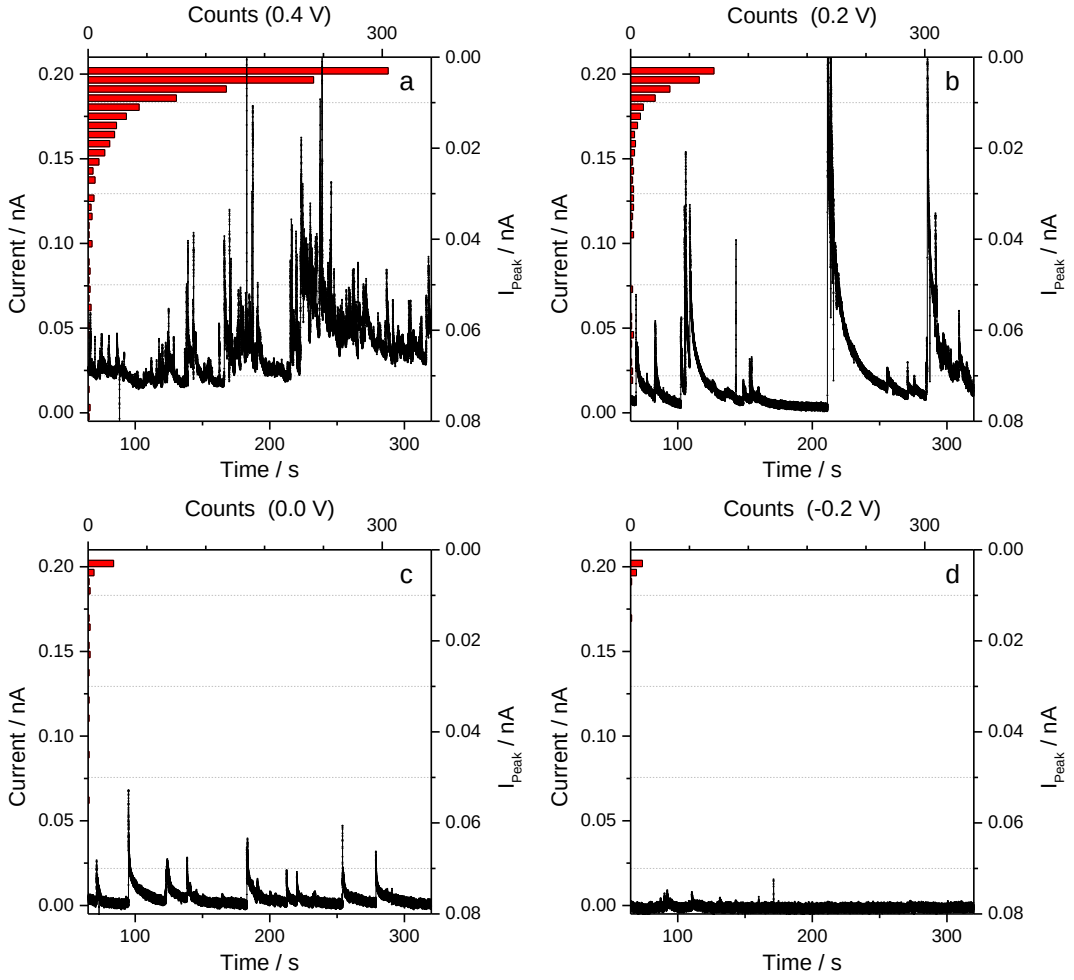

Fig. 3. Chronoamperometric responses for AuNP collisions at a carbon fibre microelectrode in N_2-saturated 0.1 M NaOH containing 5 mM glucose and 0.1 nM AuNPs, at different applied potentials (0.4, 0.2, 0 and -0.2 V, a-d respectively). Frequency plots representing spike transient maximums (overlayed) were generated by evaluation of the chronoamperometric responses presented here, which were collected with a data acquisition time of 3 ms (ca. 0.33 kHz).

Each current bin is equivalent to 2 pA.

4. Conclusion

In this work, detection of pristine AuNPs prepared by LASiS was developed based on the electrochemical nano-impact method. As these laser-ablated AuNPs exhibited electrocatalytic activities towards glucose oxidation, single nanoparticle collisions can be observed in terms of current spikes produced at the inert electrode surface. This method enables the analysis of nanoparticles without surface modification in aqueous solutions, which can provide a basis for understanding the unique properties of pristine single nanoparticles as well as those prepared by LASiS into solutions containing reagents with specific functional groups.

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