**Current topics in Physical and Nanoparticle Electrochemistry**

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**1. Introduction**

This short review covers three areas of current interest in nanoparticle research, tunnelling nanoparticle assisted electron transfer, multilayer nanostructures and some practical applications of the tunnelling phenomena described. There was no intention to cover the whole field of nanoparticle research; the topics chosen reflect some personal perceptions of the author. References to papers outside the review period have been included in some cases in order to aid understanding. The area of nanoparticle electrochemistry has been covered in recent years by three reviews dwelling on: (a) electrocatalysis, single particle studies and SECM methods [1], (b) nanoparticle collisions, nanopore and nanoparticle electrochemistry, optical detection methods and electrochemical imaging [2], and (c) a comprehensive review and analysis of nanoscale electrochemistry and techniques [3].

**2. Tunnelling electron transfer at electrochemical interfaces**

The interest in functionalised nanoparticles or MPC, is in providing readily accessible building blocks for the construction of self-assembled nanomaterials combining the properties of metals and organic compounds. The presence of a metallic core in these hybrid materials makes them suitable for incorporation into structures in which, by virtue of the large number of available electronic levels, can provide unusual electron transport properties. It has been known for a long time that electron transfer (ET) between a metal covered by alkane thiols self-assembled monolayers (SAM) and a redox species, either in solution or covalently bound to the organic backbone of the attached SAM and in direct contact with the solution, is severely hindered. For these systems, the electron transfer rate constant decreases exponentially with the thickness of the thiol layer, as might be expected for the decrease in the tunnelling probability with insulating layer thickness. However, for a dithiol SAM, the attachment of a metal nanoparticle (NP) to the distal thiol functionality results in fast electron transfer, with the attached nanoparticle acting as a short circuit to the otherwise insulating alkane layer. The properties of multilayered AuNP-thiol materials are discussed further on.

This unexpected behaviour has been known for a long time [4-6] but only recently a simple rationalisation of its origin has been presented by Chazalviel and Allongue [7] who recognised the central difference between the properties of the metal|insulator|redox couple and that of the metal|insulator|metal particle|redox couple interfaces. Employing a simple free-electron metal model, it was argued that the current is related to the electronic density of states per unit volume at the Fermi level of the electrode and to the availability of empty electronic states either on the redox species in solution (for direct metal- redox centre electron transfer) or to nanoparticles placed at the insulator-solution interface when these act as relay centres. In either case, a tunnelling factor through the insulating layer proportional to exp(-βd)(d=SAM thickness and β=tunnelling decay constant ∼ 1Å-1) must be included. Chazalviel and Allongue demonstrated that the very big difference in observed ET rate constants between the two above configurations is due to the large value of the density of states of the metal nanoparticles compared with that of a redox molecule thus making ET rates from the metal electrode to the particle many order of magnitude larger than transfers to the redox centre. Consequently, the inclusion of a metal nanoparticle can act as a “short circuit” to the insulating layer for electrochemical reactions, although no direct contact between the particles and the electrode surface takes place. ET rates are only inhibited by the presence of an insulating layer of thickness greater than a critical value.

This analysis is only valid for particles of sufficiently large dimensions so that their properties can be approximated to those of a bulk metal. For example, from current knowledge of the optical properties of Au, the mechanism of current enhancements based on free electron models is unlikely to be applicable for particle sizes below ~2 nm, i.e., for particles not displaying the typical plasmon resonance absorption peak for gold. By contrast, for the metal|insulator|redox-couple case, the potential dependence of the current is more complex and is determined by the classical relationships of activated electrochemical processes [8] in series with electron transfer by tunnelling through an insulating film.

 In classical electrochemistry experimentation, the observation of fast electron transfer reactions across an electrode covered with an insulating layer is counterintuitive. The predictions of the Chazalviel-Allongue (C.A.) theory for macroelectrodes were tested by Gooding et al [9] by investigating the dependence of electron transfer rate to the hexaamine ruthenium(III/II) aqueous redox couple across insulating films of 0.7 to 3.8 nm thickness prepared by oxidation of ethylene diamine and supporting 38 nm Au nanoparticles attached to the distal amine groups of the insulating layer. Although the particles employed were probably of irregular shape and the oxidative polymerisation of ethylene diamine would not be expected to give a good planar surface geometry for tunnelling, it is interesting to note that the dependence of the rate constant measured on insulating layer thickness was in general agreement with the predictions of the C.A. theory [7].

F. Liu, K. Khan, J.-H. Liang, J.-W. Yan, D.-Y. Wu, B.-W. Mao, P. S. Jensen, J. Zhang, and J., Ulstrup, On the Hopping Efficiency of Nanoparticles in the Electron Transfer across Self-Assembled Monolayers, ChemPhysChem, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

In an alternative analysis of this problem, Ulstrup et al [10] stressed the need to consider electron transfer through the metal|insulator|metal particle|redox couple interface as a two-step ET process, with the metal particle acting as a charge relay centre. A schematic description of the systems investigated is shown in Figure 1. The electrochemical response of the [Ru(NH3)6]2+/3+ redox couple was found invariant for Au, Pt or Pd nanoparticles attached to a dithiol layer, indicating that in this case, the rate determining step is electron transfer at the nanoparticle-solution interface and not tunnelling from the metal to the nanoparticles, the latter acting therefore as a “short circuit” i.e., a strong nanoparticle-base electrode electronic coupling, to the insulating dithiol layer (top of Figure 1). However, when ferrocene, a very fast redox group, was covalently attached to the nanoparticles (bottom of Figure 2), the measured ET rate constant depended on the metal, in the order Au>Pt>Pd. Since tunnelling across the insulating layer and ET to the Fc/Fc+ couple are consecutive processes, the rate determining state can be shifted from the former to the latter by altering the structure of the hybrid film. The very fast ET rate of the Fc/Fc+ tethered to Au nanoparticles of different dimensions has been recently demonstrated [11].

Additional confirmation of the two-step ET mechanism was obtained from measurements with different lengths of the molecular wire connecting the nanoparticles to the attached redox couple. These are important results demonstrating that although the C.A. model is basically correct, it only relates to the first electron transfer step for these hybrid structures when tunnelling rate across the insulating film is much faster than the subsequent electron transfer to the redox species in solution. Only when this situation is reversed are the full details of the ET process for different metal nanoparticles revealed [10].



**Figure 1**. Schematic illustration of ET through a metal–SAM–NP complex using two kinds of probing molecules, From F. Liu, K. Khan, J.-H. Liang, J.-W. Yan, D.-Y. Wu, B.-W. Mao, P. S. Jensen, J. Zhang, and J. Ulstrup, On the Hopping Efficiency of Nanoparticles in the Electron Transfer across Self-Assembled Monolayers, ChemPhysChem, Copyright Wiley-VCH Verlag GmbH & Co. KGaA. Reproduced with permission.

Although these questions still need some clarification, the unusual property of achieving fast electron transfer across metal|insulator|metal particle structures has opened up the possibility of employing novel substrates as electrode materials. This is important, for instance, for the development of electrochemical biosensors, where metal surface fouling can restrict the applicability of metallic electrodes. Recent work [12] has demonstrated that the use of an ethylene oxide dithiol monolayer can act as an antifouling support for Au nanoparticles. Surprisingly, ET enhancement by inclusion of a metal particle at the film-solution interface can also take place without direct covalent bond formation. Gooding et al [13] showed that by applying an external magnetic field, core shell Au@magnetite particles restored electron transfer to redox species in solution for a Au electrode otherwise passivated with an 11-mercaptoundecanoic acid SAM, by forcing the particles to contact the electrode surface.

 The enhancement of ET rates employing the metal|insulator|metal particle structure has also been demonstrated for accessing electrochemically the redox centre of enzymes. For horseradish peroxidase, the enzyme was actually reconstituted using an alkanethiol linker for connection with a 20 nm Au nanoparticle [14]. The linker carried a heme group in the distal position onto which the enzyme was reconstituted. By providing direct access to the enzyme redox centre, this elegant strategy for self-organisation of a redox enzyme-electrode surface offers interesting possibilities for establishing good electronic communication to biomolecules. The use of nanoparticles attached to a SAM to achieve long range communication between an electrode surface and a redox centre has also been demonstrated for anthraquinone attached through a C11 tether to 1.8 nm Au particles supported on a highly insulating 4,4′-biphenyl-dithiol SAM [15]. In this case, the mechanism responsible for the enhancement of ET rate constant is probably different from those analysed above due to lower density of states of the small sized nanoparticles employed and the concomitant lower concentration of free electrons as shown by the absence of the characteristic Au plasmon band for the nanoparticles employed. In addition, quantised charging effects become relevant. Nevertheless, the concept of electron shuttling to a relay centre seems to be applicable here.

Recent development in the study of nanoparticles impact on electrode surfaces has opened up a rich research field that allows the study of the electrochemical properties of individual nanoparticles in solution when colliding with an electrode poised at a potential at which an electrochemical reaction can take place [16]. Ideally, the only electron transfer reaction that can occur is that associated with the impingement of the particle with the electrode surface. During collision, the particle can act as a nanoelectrode with the consequent current amplification during the time of the contact event by electron transfer reactions with an analyte in solution. Importantly, background currents can be greatly minimised by employing the metal|insulator|metal particle structures discussed above where now the contact to a redox couple is achieved by nanoparticles in solution. This approach has been successfully developed by Bard et al. for ultramicroelectrodes coated with a thin pinhole-free insulating metal oxide dielectric and importantly, stable nanoelectrodes can be readily prepared [17]. The corresponding appropriate treatment of electrochemical kinetics for this electrode configuration has been developed [18]. This interesting experimental approach circumvents the difficult problems associated with the fabrication of nanoelectrodes and makes it possible to characterise the electrochemical properties of individual nanoparticles and nanoalloys.

**3. Tunnelling electron transfer in hybrid nanostructures.**

Multilayer metal|insulator|metal particle structures can be easily prepared by simply forming a dithiol (or other bifunctional group) SAM on nanoparticle terminated films and then attaching another layer of metal nanoparticles on to it. Since these reactions are performed by immersion of the material successively in solutions of a bifunctional ligand and of metal particles, thick hybrid films can be easily constructed [5,6,19]. There are two intriguing observations related to the electron transfer properties of these nanostructures: 1) the electron transfer to redox species in solution depends on the termination of the multilayer, either “On” when a nanoparticle is the distal species or “Off”, when the next self-assembled bifunctional layer is attached to it, and 2) electron transfer appears unhindered although the electrode-solution redox species distances involved can be of the order of 40 nm. There is a similarity with the behaviour of a single particle attached to an insulating layer and the arguments of the C.A. and Ulstrup models discussed above could be applicable. Figure 2 shows results obtained with an aqueous redox couple.



**Figure 2**. Dependence of the charge transfer resistance (*R*CT) on surface termination for multilayer hybrid structures. Bare = Au electrode; SAM = thiol terminated surface; NP = Au nanoparticle terminated structure. The values of the charge transfer resistance were obtained by AC impedance spectroscopy when the electrode was contacted with a [Ru(NH3)6]2+/3+ redox couple solution. The bifunctional linker was 11-Amino-1-undecanethiol and 12.3±0.5 nm Au particles were employed to synthesise the multilayer structure. The response clearly shows the insulting layer “short circuit” produced by the NP surface termination (see text). Based and reprinted with permission from Langmuir, 25 (2009) 11121–11128. Copyright 2009, American Chemical Society.

 These hybrid nanostructures behave as a “short circuit” between the metal and the solution. Dispersed metals incorporated within a dielectric medium are technologically very important (e.g., cermets) and have been extensively studied for over 50 years. It is interesting, then, to apply the analysis of the properties of these materials to the system described above. For instance, for the results shown in Ref. [19], for metal particle loadings below the percolation threshold where electrical conduction takes place by direct contact between the components of the dispersed metallic phase, conduction occurs mainly by tunnelling between the metallic grains with an activation energy (*E*A) given by [20,21]:

$E\_{A}=\frac{e^{2}}{8πϵε\_{0}}\left[\frac{1}{r}-\frac{1}{r+s}\right]$ (1)

ԑ is the relative dielectric permittivity of the medium in which the particles are included, ԑ0 is the permittivity of free space, *r* is the radius of the nanoparticles and *s* is the separation distance between the external radius of contiguous particles. In this example, *r* = 6.15 nm and the separation between nanoparticles was estimated as *s* = 1.6 nm from the monolayer thickness of a SAM of 11-Amino-1-undecanethiol on Au calculated by Silva et al. for Au in contact with aqueous NaClO4 [22]; ԑ = 3.6 was estimated by the same authors. From equation (1), the system described in Ref. [19] has an ET activation energy of *E*A = 6.7×10-3 eV. This very low value for the activation energy for ET across the multilayer, lower than that of the thermal energy, indicates that there is a negligible barrier for electron transfer between the base electrode and the metal clusters in contact with the solution. Similar low *E*A values for conductivity data for nanoparticle monolayers were also previously obtained by Zhong et al [23].

 The oversimplified granular metal model behind equation (1) is based on considering a purely electrostatic activation change in internal energy due to the charging energy resulting from electron transfer between a neutral nanoparticle in a matrix to produce a positive- negatively charged particle pair [20,21]. This classical theory does not attempt to analyse in detail the thermodynamics of the process responsible for the material conductivity, which would require an assessment of the Gibbs energy of activation. The analysis above provides, however, another rationalisation for the behaviour of the properties of multilayer hybrid structure as a short circuit of electron transfer to redox species in solution by highlighting a link between a well-established field in solid state physics with the electrical properties of hybrid nanostructures [23].

**4. Some current development of applications of nanoparticle tunnelling conduction.**

The application of tunnelling conduction properties of metal nanoparticle arrays to practical uses is at present attracting attention. For example, conduction in otherwise insulating metal-organic frameworks (MOF) has been achieved by controlled incorporation of silver nanocrystals within the porous structure. Importantly, a small metal loading is required for greatly improving conductivity. In this case, tunnelling between incorporated nanoparticles is responsible for electron transfer through the material, thus offering the possibility of preparing high surface nanoparticle density nanoporous electrodes without significantly impairing mass transfer to reaction centres [24], an essential requirement for their use in batteries and fuel cells. Another very interesting novel application of electron transfer across nanoparticle arrays is the development of inexpensive strain-resistance pressure devices for personalised sensors, the so-called “wearable electronics” [25]. These are based on nanoparticle arrays supported on a membrane. The membrane deformation due to pressure difference across it results in changes of interparticle separation with the corresponding change in resistance. The sensitivity of this approach is due to the exponential dependence of the tunnelling conductance on average distance between the nanoparticles in the array:

$σ=σ\_{0}e^{-βl}$ (2)

σ0 = term depending on the temperature and the organisation of the array, β = tunnelling decay constant and *l* = interparticle distance.

 For practical applications, an uncertainty in the measured conductivity of nanoparticle monolayers is the degree of order of the sample. Yang and Hallinan [26] developed a simple technique to obtain highly organised layers over large areas by the two-phase reaction of aqueous citrate particles stabilised with alkylamines dissolved in *n*–hexane. The monolayer protected particles produced by displacement of the stabilising citrate ion by the amine formed a robust and highly ordered monolayer at the aqueous-organic liquid-liquid interface that could be easily separated for further studies. The 2-D films produced were analysed by TEM and Grazing Incidence Small Angle X-ray Scattering demonstrating that the self-organised films had very long range order. The measured tunnelling decay constant for these structures was β = 0.26 Å−1 [27] that should be compared with a value of β = 0.85 Å−1 from single molecule measurements using thiols with 6, 8 and 10 methylene groups [28]. Yang et al. [27] proposed that this low value of β obtained results from the various parallel electron transfer pathways possible when measuring the conductance of an array.



**Figure 3.** Principle of operation of strain sensitive nanoparticle tunnelling devices. PET/MPTS is a flexible polyethylene terephthalate film functionalised with (3-mercaptopropyl)trimethoxysilane to aid Ag nanoparticles attachment. Strain applied to the film results in an increase of the average separation distance between nanoparticles and hence changes in the tunnelling current. The ~~central~~ figure has been reproduced from Ref. [30] with permission from the Royal Society of Chemistry. See text for details.

Bending sensors based on these thin film nanoparticle tunnelling devices have been developed and used, for example, for monitoring neck muscle motion during speech or finger joint bending motions [29]. Lee et al [30] fabricated a sensitive multiarray device by photolithography using Ag nanoparticles attached to a polyethylene terephthalate film as a flexible support. Vossmeyer et al [31] followed a different strategy, avoiding the use of a support for the nanoparticles for building the sensing component of a pressure sensor by using gold nanoparticles themselves both as a constituent of the stress sensing membrane and providing, at the same time, the electromechanical conversion of pressure variation into electrical signals by virtue of the changes in metal particle separation caused by the flexing of the membrane under pressure differences. These developments provide a novel approach for applications in portable devices.

**5. Concluding remarks**

Although synthetic procedures for functionalised metallic nanoparticles are now well-established, it is only recently that detailed structural information has become available, for example, for thiolated metal particles, from x-ray diffraction studies and importantly, from an understanding of the nature of the Au-S bond in these materials [32]. These advances are providing a solid foundation for the development of practical uses. Biomedical applications are attracting a great deal of interest by employing the combination of a metal core with specific functional groups attached to it. Besides the examples given in this review, their use as drug delivery systems in photodynamic therapy for cancer treatment offer unusual advantages by the incorporation of photosensitiser ligands in plasmonic nanoparticles [33]. Another important area that has not been included in this review due to space limitations is the application of nanoalloys in electrocatalysis. The challenge here is to design nanoalloys that combine a base metal such as Au with an alloying component that can provide specific surface reaction centres of predictive properties [34].

 The rapid developments in the area of nanoparticle applications are a clear demonstration of the advances that can be achieved by interdisciplinary research and by blending quantum chemical calculations, experimentation and modern microfabrication techniques.

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