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Charge injection and lateral conductivity in monolayers of metallic nanoparticles

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Scanning electrochemical microscopy has been used to quantify both the charge injection energetics between a solution redox couple and a monolayer of hexanethiol stabilised gold nanoparticles and the subsequent lateral charge transport in the monolayer.

Monolayer-protected clusters (MPCs) have attracted wide interest due to their unique electronic and chemical properties that depend critically on the nanoparticle size and nature of the protecting layer.[1] Electrochemical properties of MPCs have been probed both in solution,[2] Langmuir monolayers,[3] and in mono-[4] and multilayer films on electrodes.[4a,4e,5] However, an experimental arrangement where the nanoparticles are deposited onto an electrode surface does not allow the lateral conductivity of the film to be investigated. This obstacle can be circumvented by the use of scanning electrochemical microscopy (SECM), which has been applied to probe the lateral diffusion of protons along stearic acid monolayers,[6] lateral charge hopping in redox active monolayers[7] or polyaniline ultra-thin films[8] and metal–insulator transition in Ag nanoparticle monolayers.[9] Also, electrocatalytic properties of gold nanoparticle films have recently been demonstrated using SECM.[10] Essentially, SECM involves electrolysis of a solution redox mediator at a microelectrode (SECM tip), and monitoring the resulting tip current as a function of the tip–substrate distance. Using a suitable model for the corresponding transport problem, experimental approach curves yield quantitative information on the processes occurring at the substrate.

This communication describes quantitative SECM experiments that probe both the electron injection from a nanoparticle film to a solution redox couple and the subsequent lateral charge transport in the monolayer. To this end, monolayers of hexanethiol stabilised gold nanoparticles[1d,2d] were deposited on glass microscope slides by the Langmuir–Schaefer method.† Subsequently, a drop of the aqueous phase was pipetted onto the slide to give the experimental arrangement depicted in Fig. 1, allowing SECM investigation of the MPC film.‡ The nanoparticles used in this study are sufficiently small to undergo quantised double charging (average spacing between subsequent charge injections was *ca.* 250 mV) and thus, can be considered as multivalent redox species.[1a,2b,2d] The inset in Fig. 1 shows the relevant redox states of the particles and the solution redox couple. The solution redox couple "fixes" the potential of the film to a value at the foot of the FcMeOH → $FcMeOH^+$ oxidation wave, which is assigned charge state *z* in Fig. 1. The tip generated $FcMeOH^+$ will oxidise the nanoparticles in the film to the charge state *z*+1, setting up a redox state gradient in the film, which in turn results in lateral charge transport.

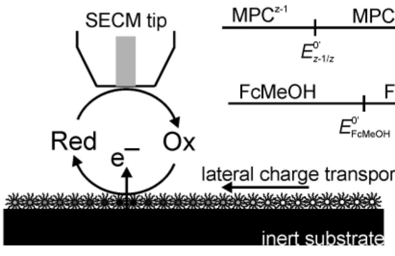

Fig. 1 Schematic of the SECM setup. Inset shows the relation between the standard potentials of the solution redox couple and the nanoparticles in the film.

At steady-state, the observed SECM response will be a combination of the diffusion flux in the solution and the flux due to lateral charge transport in the film. The diffusion flux is directly proportional to the concentration of the redox mediator in solution. This implies that in order to observe lateral transport, the concentration of the redox mediator has to be reduced sufficiently. In practice, with the nanoparticle monolayers described here, "sufficiently low" concentration refers to micromolar range, typically between 1 and 10 μmol dm^{-3}. Typical examples of approach curves obtained to the MPC monolayer at suitable redox mediator concentration are given in Fig. 2. At these very low concentrations and currents (limiting currents typically 3 to 20 pA), caution has to be exercised to ensure that the observed response is due to the proposed mechanism and not an experimental artefact.§ It must be emphasised that the positive feedback response given in Fig. 2 was never observed in the absence of the MPC film for all concentrations used in this study. The observed response strongly resembles that for a drop-cast nanoparticle film (higher conductivity of the film) at a higher solution redox couple concentration (data not shown), which further verifies that the feedback response is due to charge transport in the film.

The SECM response in feedback mode can be modelled similarly to the previous charge hopping studies.[7,8] It was realised, however, that in order to reproduce the observed response, the reaction had to be treated as reversible. The

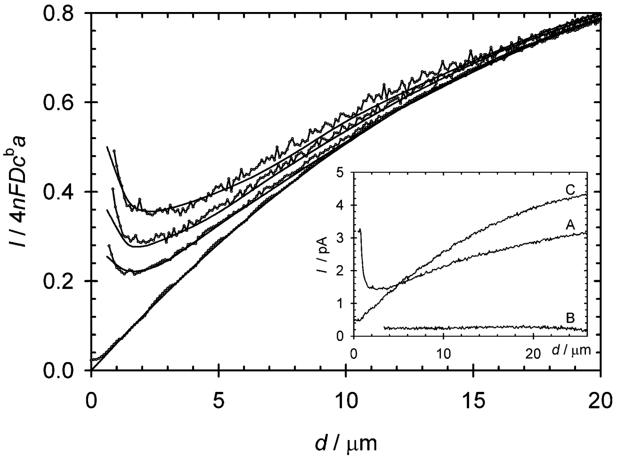

Fig. 2 Experimental and theoretical (with the parameters described in the text) approach curves (normalised current *vs.* the tip–substrate distance) to a monolayer of hexanethiol stabilised gold nanoparticles at different bulk concentrations of the redox mediator, from top to bottom 1.0, 1.5, and 2.8 μmol dm^{-3}. Lowest curve for 0.11 mM FcMeOH together with the theoretical response for an insulating substrate. Inset: Raw experimental approach curves to the monolayer for (A) 1.0 and (B) 0 μmol dm^{-3} FcMeOH. (C) shows the response for an approach to a bare glass slide.

substrate boundary condition is then given by eqn. (1),

$$\left.\frac{\partial C}{\partial Z}\right|_{Z=L} = K_{\mathrm{f}}\left(1-C\right)\theta - K_{\mathrm{b}}C\left(1-\theta\right) \quad (1)$$

where $L = d/a$ is the dimensionless tip–substrate distance, $C = c_{\mathrm{red}}/c^{\mathrm{b}}$, c^{b} the bulk concentration of the redox mediator, a the electrode radius, $K_{\mathrm{f}} = k_{\mathrm{f}}\Gamma_{\mathrm{max}}a/D_{\mathrm{soln}}$ and $K_{\mathrm{b}} = k_{\mathrm{b}}\Gamma_{\mathrm{max}}a/D_{\mathrm{soln}}$ are the dimensionless forward and reverse rate constants, Γ_{max} is the total surface concentration of the nanoparticles, D_{soln} the diffusion coefficient of the solution redox couple and $\theta = \Gamma_{\mathrm{MPC}(z)}/\Gamma_{\mathrm{max}}$, where $\Gamma_{\mathrm{MPC}(z)}$ is the surface concentration of the nanoparticles at charge state z. The boundary condition (1) is coupled to a surface diffusion equation, eqn. (2),

$$\frac{\partial^2\theta}{\partial R^2} + \frac{1}{R}\frac{\partial\theta}{\partial R} - \frac{1}{\gamma D_{\mathrm{r}}}\left(K_{\mathrm{f}}\left(1-C\right)\theta - K_{\mathrm{b}}C\left(1-\theta\right)\right) = 0 \quad (2)$$

where $\gamma = \Gamma_{\mathrm{max}}/(c^{\mathrm{b}}a)$ and $D_{\mathrm{r}} = D_{\mathrm{surf}}/D_{\mathrm{soln}}$ where D_{surf} is the electron hopping diffusion coefficient. Eqns. (1) and (2) assume that the lateral transport occurs *via* a diffusion mechanism and that there is no electrical potential gradient in the film. The validity of these assumptions will be tested in a subsequent publication. The resulting non-linear diffusion problem was solved using an adaptively refined finite element method as implemented in finite element toolbox FEMLAB (Comsol Ab, Sweden).

Some approach curves and the corresponding fits to the theory are shown in Fig. 2. As the concentration of the solution redox mediator is lowered sufficiently, positive feedback is obtained due to the lateral charge transport in the monolayer. The theoretical expressions were generated using $K = K_{\mathrm{f}}/K_{\mathrm{b}} = 0.01$ (no kinetic limitations could be detected), and, from top to bottom, $\gamma D_{\mathrm{r}} = 2.8$, 1.6, and 0.8. The lowest theoretical curve is the response for an insulating substrate (high concentration of solution redox mediator and/or the absence of monolayer). Theoretically, the value of K affects the shape of the approach curve and the value of γD_{r} controls the amount of positive feedback.

The value of K reflects the difference between the standard redox potentials of the solution and monolayer redox species, and it can be expressed in terms of the Nernst equation for the electron transfer reaction: $K = \exp(F/(RT)\Delta E^{0\prime})$ where $\Delta E^{0\prime} = E^{0\prime}_{\mathrm{FcMeOH}} - E^{0\prime}_{z/z+1}$. Using the value of K obtained from fitting experimental curves to theoretical predictions, we obtain $\Delta E^{0\prime} = -120$ mV. This value is in-line with the value obtained from voltammetric measurements of the nanoparticles in 1,2-dichloroethane (*ca.* −100 mV). Direct comparison is impossible, however, as the redox potentials of the nanoparticles depend on the local dielectric environment, which is different in a monolayer and in an organic solution.[4d,4g]

The value of γD_{r} as a function of $1/c^{\mathrm{b}}$ gives $(\Gamma_{\mathrm{max}}/a)(D_{\mathrm{surf}}/D_{\mathrm{soln}}) = 2.3$ μmol dm^{-3} which can be used to estimate the surface diffusion coefficient given the values of the surface coverage (from the Langmuir isotherm, $\Gamma_{\mathrm{max}} = 3.3 \times 10^{-11}$ mol cm^{-2}) and the diffusion coefficient of the redox mediator ($D_{\mathrm{soln}} = 7 \times 10^{-6}$ cm^2 s^{-1}): $D_{\mathrm{surf}} = 5 \times 10^{-7}$ cm^2 s^{-1}. This value can be correlated to the first order rate constant, k, for electron transfer between the nanoparticles using the Dahms–Ruff formalism:[11] $D_{\mathrm{surf}} = k\delta^2/4$ where δ is the charge hopping distance in the monolayer, *i.e.* the core–core spacing. Assuming hexagonal packing of the monolayer, δ can be estimated as $\delta = 0.8$ nm, which gives $k = 3 \times 10^8$ s^{-1}. This compares well with the values reported in the literature for drop-cast layers of hexanethiol stabilised nanoparticles.[5c]

In conclusion, we have demonstrated measurement of the charge injection energetics from a solution redox couple into a nanoparticle monolayer and the subsequent lateral charge transport using scanning electrochemical microscopy. It was shown that it is possible to separate these two phenomena in a quantitative fashion. Further work using different redox couples at different mono- and multilayer assemblies of MPCs is in progress and will be reported in due course.

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Notes and references

† The particles (core diameter 1.6 nm) were spread from a 1 mg ml^{-1} solution in chloroform onto a pure water (milli-Q, Millipore) subphase. The deposition surface pressure was 15 mN m^{-1} (collapse pressure was *ca.* 20 mN m^{-1}) with a compression rate of 5 mm min^{-1}. After relaxation of the monolayer (30 min), a glass slide was brought down horizontally to touch the monolayer by hand and lifted carefully after a contact time of a few seconds.

‡ The aqueous phase contained varying concentrations of ferrocenemethanol (FcMeOH, Aldrich) and 100 mM LiCl as base electrolyte. SECM (CHI900, CH-Instruments, Austin, Texas) experiments used a 25 μm diameter Pt microelectrode (overall tip diameter relative to the electrode diameter, $R_{\mathrm{g}} = 7.5$) as the tip and a Ag/AgCl wire served both as counter and reference electrodes. The SECM approach curves were carried out at an approach speed of 1 μm s^{-1}.

§ Approach curves were always also recorded both in the absence of the redox couple and to a bare glass substrate in the concentration range of the redox mediator used (see inset in Fig. 2). The background measurement was performed by exchanging the solution with one containing base electrolyte only and repeating the experiment. All approach curves were corrected for the background response.

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