

Electron transfer reactions at gold nanoparticles

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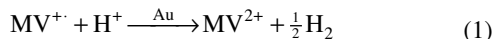
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It is demonstrated that scanning electrochemical microscopy can be used to investigate the kinetics of electron transfer reactions catalysed by metal nanoparticles supported on an insulating substrate.

The study of single electron transfer events at nanoparticles is of great interest for understanding the structure and properties of artificial atoms and quantum dots.¹ The electronic properties of metals are greatly changed as size decreases and the metal–insulator transition is approached.² Murray *et al.*³ recently observed quantum size effects in an electrochemical study of electron transfer (ET) in layers of thiol capped nanoparticles. The influence of size on rates of ET (*e.g.* how the density of states alters kinetics) is difficult to investigate when the substrate itself can support ET reactions. Here we demonstrate how this problem can be circumvented by the use of scanning electrochemical microscopy (SECM), when the nanoparticles are supported on an insulating substrate.

SECM is a powerful method for the study of reaction kinetics at a wide range of interfaces⁴ and the technique has recently been employed to study rate constants of ET reactions catalysed by a 25 μm diameter disc metal microelectrode.⁵ In the present work, the hydrogen evolution reaction mediated by gold nanoparticles attached to a non-conducting glass surface has been investigated. The overall reaction studied is:



MV^{2+} and MV^+ are methyl viologen and its radical cation, respectively.

Underivatized gold nanoparticles (mean diameter 6 nm) were prepared by the two-phase method described in ref. 6. Microscope slides were cleaned and then silanised with 3-mercaptopropyltrimethoxysilane following the method of Goss *et al.*⁷ The silanised slides were immersed in a toluene solution of Au nanoparticles for different periods of time. Fig. 1 shows UV-visible spectra for Au nanoparticles in toluene (curve a) and attached to both sides of a slide (curves b and c). The spectrum in toluene features the typical plasmon absorbance maximum at 520 nm, which shifts to approximately 580 nm when the particles are attached to glass due to changes in the dielectric environment. Increasing the immersion time enhances coverage as shown by the increase in absorbance. The presence of nanoparticles on the substrate was further confirmed using intermittent contact mode AFM. For the substrates corresponding to b and c in Fig. 1, particle densities, Γ_{Au} , of 900 (± 200) μm^{-2} and 1800 (± 400) μm^{-2} were determined.

SECM utilises an ultramicroelectrode (UME) tip to generate a reactant and to monitor interfacial reactions *via* the current response as the tip is brought in close proximity to a substrate⁸ (Fig. 2). The amount of tip-generated MV^+ consumed at the nanoparticle film, and hence the measured steady-state current, i , compared to the value when the UME is far away from the surface, $i(\infty)$, depends on the rate of reaction (1). In acid solutions, the redox potential of the $\text{MV}^{2+}/\text{MV}^+$ couple is more negative than that of the H_2/H^+ couple and so reaction (1) is thermodynamically possible. A Hg film UME was used as the

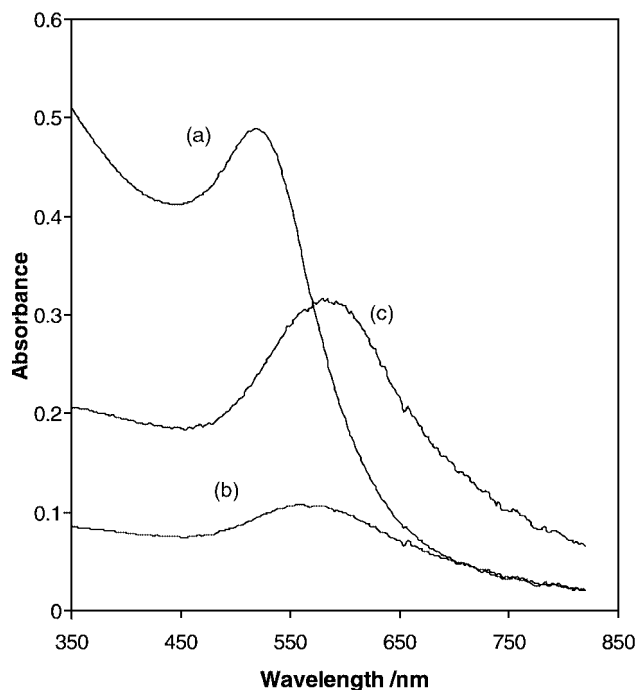


Fig. 1 UV-visible spectra of Au nanoparticles in (a) toluene and on a silanised glass slide soaked in a nanoparticle solution for 1 (b) and 19 (c) hours.

tip working electrode, so that only currents due to the viologen couple were measured. The aqueous phase contained 1 mM MV^{2+} and 0.1 M buffer, with MV^+ generated at the tip by reduction of MV^{2+} . MV^+ diffused to the nanoparticle film where it reduced H^+ at the nanoparticle–solution interface. The regenerated MV^{2+} diffused back to the Hg UME, thereby enhancing the current.

The SECM current response was calculated as a function of distance, d , between the UME and substrate using a simple kinetic model. Considering that discharge is the rate-limiting step for hydrogen evolution on metal surfaces,^{5,9} and neglecting the reverse reaction between hydrogen and MV^{2+} , the following rate law is considered:

$$\text{rate} = \Gamma_{\text{Au}} [\text{H}^+]^m k' e^{-\frac{nF}{RT}\eta} \quad (2)$$

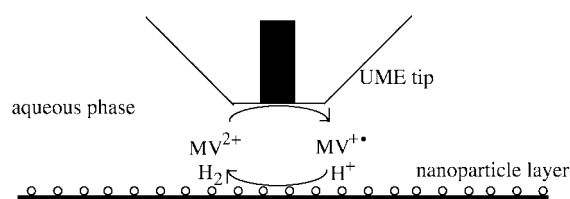


Fig. 2 Schematic (not to scale) of the experimental arrangement.

where k' including the effective surface area per cluster is a constant, m is the reaction order with respect to H^+ , α is the electron transfer coefficient for proton reduction, n is the number of electrons transferred, F is Faraday's constant and η is the overpotential for hydrogen evolution. R and T have their usual meaning. The overpotential is given by,

$$\eta = \left(E_{MV^{2+}/MV^+}^{0'} - E_{H^+/H_2} \right) + \frac{RT}{nF} \ln \frac{[MV^{2+}]_{\text{surf}}}{[MV^+]_{\text{surf}}} \quad (3)$$

where $E_{MV^{2+}/MV^+}^{0'}$ is the formal potential for the methyl viologen couple and E_{H^+/H_2} is the pH-dependent potential for the H^+/H_2 couple. From eqns. (2) and (3) and assuming $\alpha = 0.5$,

$$\text{rate} = \Gamma_{\text{Au}} ([H^+])^m k'' \sqrt{\frac{[MV^+]_{\text{surf}}}{[MV^{2+}]_{\text{surf}}}} \quad (4)$$

where k'' is a constant. Reaction (1) could only be observed when the pH was relatively low (*vide infra*). Since the kinetics of hydrogen evolution is slow and the system is buffered, $[H^+]$ is a constant. The boundary condition at the substrate for the SECM experiment is therefore:

$$D \frac{\partial [MV^{2+}]}{\partial z} = k''' \sqrt{\frac{[MV^+]_{\text{surf}}}{[MV^{2+}]_{\text{surf}}}} \quad (5)$$

where D is the diffusion coefficient of both MV^{2+} and MV^+ , taken as equal.

The diffusion equations for the redox species in solution were solved numerically in the axisymmetric cylindrical geometry (r , z co-ordinates starting from the centre of the UME) of SECM with the usual conditions.¹⁰

A diffusion coefficient for MV^{2+} of $8.0 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ was measured by steady-state linear sweep voltammetry and potential step chronoamperometry¹¹ and used in the simulation of SECM approach curves, shown in Fig. 3. At pH 7, the approach curve with gold particles on the substrate is indistinguishable from that for a naked glass surface. This is expected considering the similarity of the potentials $E_{H^+/H_2} = -0.414$ (pH = 7) and $E_{MV^{2+}/MV^+} = -0.446 \text{ V}$ ¹² and the

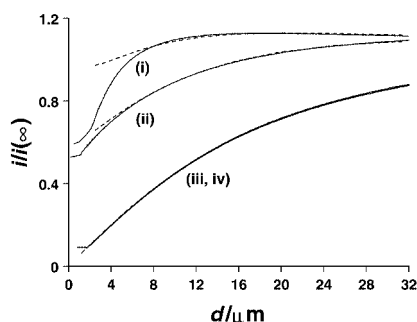


Fig. 3 SECM approach curves for reaction (1) at the substrate. From top to bottom the solid lines are experimental data for: (i) $\Gamma_{\text{Au}} = 1800 (\pm 400) \mu\text{m}^{-2}$ (pH = 2), (ii) $\Gamma_{\text{Au}} = 900 (\pm 200) \mu\text{m}^{-2}$ (pH = 2), and (iii) $\Gamma_{\text{Au}} = 1800 (\pm 400) \mu\text{m}^{-2}$ (pH = 7). The latter solid line is co-incident with the approach curve for an inert substrate (iv), naked glass surface; pH = 2 and 7). From top to bottom, the dashed theoretical curves are for $k''' = 3.5 \times 10^{-9}$, 1.5×10^{-9} and $0 \text{ mol cm}^{-2} \text{ s}^{-1}$.

sluggish kinetics for hydrogen evolution. Crucially, this result also demonstrates that the Au nanoparticles are not in electrical contact creating a macroscopic film, otherwise positive feedback would have been observed with the reversible methyl viologen couple.¹³

The data at pH 2 show conclusively that reaction (1) takes place on the nanoparticles and these results are corroborated by the further enhancement in current as Γ_{Au} is increased (Fig. 3). The experimental curves are seen to be in good agreement with theory, except at the closest distances where the feedback currents indicate a smaller interfacial reaction flux than predicted. This is most likely because the product, H_2 , can only escape the SECM tip-substrate geometry by restricted diffusion and so accumulates, thereby promoting the back reaction.¹⁴ The rate constants obtained from the simulations were 1.5×10^{-9} and $3.5 \times 10^{-9} \text{ mol cm}^{-2} \text{ s}^{-1}$, in agreement with the change in particle density by a factor of two measured by AFM and consistent with the absorbance ratio of approximately three between the two films. When the potential at the substrate is set by an equal concentration of MV^{2+} and MV^+ , the data correspond to a hydrogen discharge rate of $(6 \pm 1) \times 10^3$ molecules of H_2 per second per particle.

We have demonstrated a method for measuring rates of ET reactions for immobilised nanoparticles that does not require electronic connectivity with the substrate. The importance of this method is twofold: (i) it gives the possibility of investigating size effects on kinetics of reactions occurring on nanostructures and (ii) the study of reactions at semiconductor nanoparticle surfaces in the absence of a metallic conductor becomes accessible.

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