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On the Origin of the Efficient Nanoparticle Mediated Electron Transfer across a Self-Assembled Monolayer

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S *Supporting Information*

ABSTRACT: Recent advances in bioelectrochemistry came from the elaboration of conducting electrodes modified by an organic layer onto which nanoparticles are adsorbed. Self-assembled monolayers on noble-metal electrodes are known to hinder the electrochemical kinetics of fast-transfer redox systems. Surprisingly, fast kinetics are recovered when metal nanoparticles are deposited on top of the monolayer. We show that this surprising behavior can be fully accounted for when realizing that electron transfer from metal to metal is intrinsically easier than transfer between metal and redox system by many orders of magnitude.

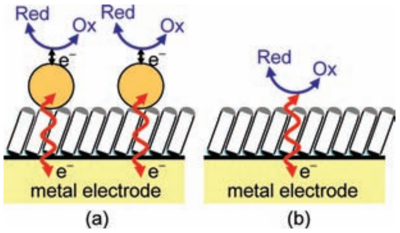

Figure 1. Scheme of the two constructs compared here. (a) ET across a SAM mediated by gold nanoparticles. (b) ET across the bare SAM.

In this communication, we present a simple theoretical argument that explains the efficient electrochemical electron transfer (ET) observed in many advanced bioelectrochemical systems based on a conducting electrode modified by an organic layer with adsorbed metal or semiconductor nanoparticles (NP) (for reviews, see[1−3]). Here we restrict the demonstration to a simple construct (Figure 1a), consisting of a metal substrate modified with a self-assembled monolayer (SAM) onto which metal NPs are adsorbed. This enables us to compare our theoretical predictions with existing experimental data obtained in different groups.[4−7] However, the argument discussed below is very general and applies, for instance, to semiconductor electrodes[8] or other types of nanoparticles, such as carbon nanotubes (CNT)[9] for which observations are very similar.

The group of Natan showed very early that an electrode composed of gold NPs adsorbed on a thin organic layer behaves like a bulk gold electrode.[10] Very recently, the groups of Fermin[4−6] and Gooding[7] considered similar systems in great detail to investigate nanoparticle-mediated ET across an organic layer. In particular, they compared ET with that at the corresponding modified electrode with no adsorbed NPs (Figure 1b). In the absence of gold nanoparticles, they found the expected law $i \propto \exp(-\beta d)$ where $\beta \sim 1$ Å^{-1} for saturated molecular chains[11] and established that adsorption of NPs leads to ET *as efficient as* on the bare gold electrode (Figure 1a) because the measured voltammogram was identical to that of a bare surface. Remarkably, NP-mediated ET appears distance independent, i.e. independent of the thickness of the organic film. In the case of SAMs of alkane thiols, no chain-length dependence was measured from $n = 2$ to 10, where n is the number of $-CH_2$ units per chain.[7] In the case of polyelectrolyte multilayers (PM),[4−6] even longer-range ET is observed, up to film thicknesses of 6.5 nm. Moreover, a very small NP coverage (a few %) is sufficient to promote efficient electrochemical transfer.[6] Also, noticeably, the NPs diameter seems to have no sizable impact on ET in the range 12−20 nm. Finally, when multiple thiol and NP layers are deposited, it turns out that the ET rate depends only on the nature of the final step (thiolation or gold-nanoparticles deposition). The above phenomenon appears quite general since similar observations were reported with different systems involving other types of substrates or NPs. These works are reviewed in the introduction of ref 7.

A critical point of concern in these experiments is the possible occurrence of short circuits between some NPs and the gold substrate, because some of the NPs may adsorb onto structural defects of the organic film. This point was carefully addressed and was discarded in the above cited studies.[6,7] Penetration of the NPs into the SAM (at well-defined molecular domains) could be another source of short circuits because the NP adsorption induces some mechanical deformation of the SAM. An estimate of the penetration depth can be derived from experiments using conductive AFM tips, whose radius of curvature is similar to that of the NP radius.[12,13] Transport measurements clearly indicate that the tip may come into contact with the substrate if the applied force is at least 100 nN for molecular chains with more than 12 methylene units.[13] Such a force is 1 order of magnitude larger than any other forces exerted by the NP onto the SAM. Electrostatic forces are only ∼1 nN,[12] adhesion forces are in the range 10−15 nN,[12,13] and the metal−metal van der Waals attraction remains also below 10 nN (for a NP radius $R = 10$ nm and a SAM thickness $d = 1$ nm). These considerations explain that the contact resistance is $R = R_0\exp(\beta d)$ for forces below 20 nN (d is the SAM thickness and $\beta \sim 1$ Å^{-1} for alkyl chains).[12]

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Hence, all in all, there is strong evidence that, in ref 7, the electron transfer has to take place across the SAM. In addition, the survival of an efficient transfer for (PM) systems[6] and multilayers[7] stands as a strong argument against any explanation in terms of total or even partial penetration of NPs into the SAM. The efficient NP-mediated ET (case of Figure 1a) has been attributed to "hot" or "resonant" electrochemical transfer between the NP and the redox species in solution,[4,6] without providing any convincing theoretical background.

In this contribution, by using very simple arguments, it will be shown that an efficient ET at metal/SAM/nanoparticles electrodes is perfectly consistent with the orders of magnitude for the electron transfer processes between the two metal phases and the redox system, and fully compatible with the present understanding of charge transfer at interfaces.[11] As shown below, the key point is that electron transfer between two metallic phases under an applied potential difference is by far easier than electron transfer between a metal and a dilute redox species in solution.

For a simple outer-sphere reorganization redox system, the current density at a bare electrode can be written under the form[14]

$$J_{\text{M-redox}} = J_0(e^{qV/2k_BT} - e^{-qV/2k_BT}) \tag{1}$$

where q is elementary charge, V overpotential, T absolute temperature, k_B Boltzmann's constant, and J_0 an exchange current density, on the order of 1−10 mA/cm^2. For $q|V| \ll k_BT$, eq 1 can be linearized as $J_{\text{M-redox}} \approx J_0\, qV/k_BT$. On the other hand, upon applying a potential difference V between two metals (or two pieces of a same metal), the current density can be estimated by counting the number of electrons able to jump from occupied states in the negatively polarized metal to empty states in the other metal. Taking the ideal case of a free-electron metal with Fermi energy E_F, for small V this can be written, in a simple gas-kinetic-theory approach:

$$J_{\text{M-M}} = \rho(E_F)qV \times \frac{qv_F}{4} \times p \tag{2}$$

where $\rho(E_F)$ is the electron density of states per unit volume at the Fermi level, $\rho(E_F)qV$ is the number of electrons per unit volume whose transfer is energetically allowed, v_F is the Fermi velocity, qv_F is the contribution to the current density of an electron impinging onto the interface under normal incidence, and the 1/4 factor comes from angular averaging.[15] A dimensionless factor p has been added to this otherwise semiclassical expression in order to take into account the quantum-mechanical reflection probability. For two metals in near contact, p is on the order of unity, and eq 2 can be rewritten under a form comparable to the linearized form of eq 1:

$$J_{\text{M-M}} = J_1\frac{qV}{k_BT}, \quad \text{with}$$

$$J_1 = \rho(E_F)k_BT\frac{qv_F}{4} = \frac{k_BTqk_F^2}{4\pi^2\hbar} \sim 10^9 - 10^{10}\,\text{A/cm}^2 \tag{3}$$

where $\hbar$ has its usual meaning, and we have used the known relations for a free-electron metal [$\rho(E_F) = 3n/2E_F$, electron concentration $n = k_F^3/3\pi^2$, and Fermi wavevector $k_F \sim 10^8$ cm^{-1}]. This estimate of $J_1 \sim 10^9$−10^{10} A/cm^2 is roughly consistent with the preexponential factor (~10^8 A/cm^2) found experimentally in the measurement of current−voltage characteristics of gold/SAM/mercury structures.[16] Notice that J_1 is larger than J_0 by about *12 orders of magnitude*.

The above estimate holds for electron transfer across a SAM sandwiched between two metal layers. We now consider metal/SAM and metal/SAM/metal electrodes. In either case the exchange current density across the SAM (J_0 or J_1, respectively) must be multiplied by the tunneling factor $\sim \exp(-\beta d)$, where d is the SAM thickness and $\beta \sim 10^7$−10^8 cm^{-1}.[11] However the practical consequences are quite different in the two configurations: In the absence of the metal overlayer on top of the SAM, the potential/current density relation can be rewritten after eq 1, where J_0 has now been replaced by $J_0 \exp(-\beta d)$:

$$V = \frac{2k_BT}{q}\sinh^{-1}\left(\frac{J}{2J_0\exp(-\beta d)}\right) \tag{4}$$

Typically, $\exp(-\beta d)$ is on the order of 10^{-5} for alkyl chains with 10 carbons, leading to an exchange current density of 10−100 nA/cm^2. As a consequence of eq 4, flowing currents larger than only a few μA/cm^2 require applying a large overpotential, which perfectly accounts for the observed flattening of the voltammograms in the case of Figure 1b. In the presence of a metal layer on top of the SAM, the potential is the sum of two terms (electrochemical interface + potential drop across the insulating layer):

$$V = \frac{k_BT}{q}\left[2\sinh^{-1}\left(\frac{J}{2J_0}\right) + \frac{J}{J_1\exp(-\beta d)}\right] \tag{5}$$

In this case, the effect of the organic layer (case of alkane chains) is limited to the second term, which remains negligible, because J_1 is so huge that $J_1 \exp(-\beta d)$ is still much larger than J and J_0. As a result, a metal/thin-insulator/metal stack amounts to an effective short-circuit, and the potential applied to the electrode appears almost entirely at the top metal layer/electrolyte interface.

Bioelectrochemical systems are based on the use of metal NPs. Locally, the ET is as above unless the NPs are very small. How small must be the NPs to affect ET? For a NP in contact with an electrolyte, an activation barrier will appear, corresponding to the reorganization of the embedding medium upon changing the charge state of the NP. This effect may be described by the well-known Marcus−Gerischer−Morrison theory, in the same way as for a redox species in solution.[14,17,18] For a NP of radius a, the reorganization energy writes $\lambda = q^2/4\pi\varepsilon_0 a$, where ε_0 is vacuum permittivity, and the above exchange current density J_1 must be corrected by a multiplicative factor on the order of $\exp(-\lambda/4k_BT)$. Taking, as an extreme case, a NP of diameter $2a = 3$ nm, one has $\lambda \approx 1$ eV, $\exp(-\lambda/4k_BT) \sim 10^{-4}$, and J_1 is now "only" on the order of 10^5−10^6 A/cm^2. This is still 7 orders of magnitude as large as J_0, and the J_1/J_0 ratio will remain huge enough to explain that NP-mediated ET remains efficient.

Hence, the present argument lifts the paradox of the efficient NP-mediated ET. It explains its insensitivity to the organic layer thickness (which may be insulating), as well as to the gold-particle diameter. It explains further that a subsurface coverage is sufficient to promote efficient ET (for 10% coverage this only affects J_1 by another factor ~10^{-1}). The ET becomes affected when $J_1 \exp(-\lambda/4k_BT) \exp(-\beta d) < J_0$, which requires specific conditions. Assuming typical values $J_1/J_0 = 10^{12}$ and $\beta d_0 = 1$, where d_0 is the thickness corresponding to a CH$_2$ unit, the solid line in Figure 2 defines the transition between the two regimes.

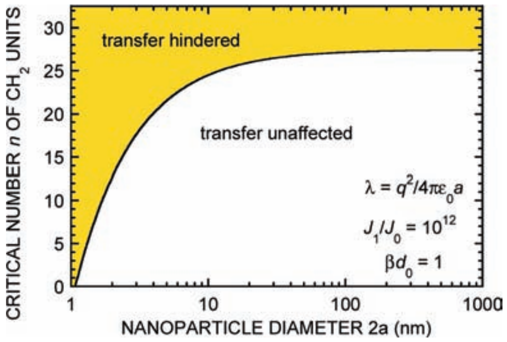

Figure 2. Critical number n of CH_2 units above which a SAM coated with gold nanoparticles is expected to lead to a change in the voltammogram of a reversible redox system in solution (shaded area) as compared to that obtained on a bare gold electrode. The equation for the line is $J_1 \exp(-\lambda/4k_BT) \exp(-\beta d_0 n) = J_0$. Note that the clear area below the critical line encompasses the whole range of published experiments.

Below the solid line, efficient NP-mediated ET is expected. The experimental conditions used in the literature are all in this region. Deviations from this behavior require sufficiently thick SAMs (to make $\exp(-\beta d)$ sufficiently small) or very small nanoparticles (this lowers the effective value of J_1/J_0, due to the reorganization energy λ). Note that Coulombic blockade effects may also appear for $q^2/(4\pi a^2 C_H) \gtrsim k_BT$, where C_H is double-layer capacitance. This may occur for very small NPs (~1 nm), a size below which size quantization may also become important. However, such effects would appear only for very monodisperse NPs, since a few particles larger than the critical size may be sufficient to provide an efficient parallel communication channel.

A detailed inspection of the theory for J_0, which is out of the scope of this short communication, indicates that the small value of J_0 as compared to that of J_1 arises from several factors: low equivalent surface concentration of redox species within a tunneling distance from the surface, due to their dilution in solution, availability of a continuum of states in the metal as compared to a single level for a redox species, lower electron coupling between metal and redox species than between metal and metal. In any case, the conclusions derived from Figure 2 remain valid for fast redox systems at any practical concentration.

To summarize, one must keep in mind that electron transfer at a sandwich structure metal/insulator/metal may be many orders of magnitude (~10^{12}!) more efficient than electron transfer between a metal and redox species in solution. This fact perfectly explains the efficient NP-mediated ET at metal/SAM/NPs electrodes. Deviations from this behavior are only expected in specific conditions which have been discussed above. Realizing this fact allows one to understand the—at first sight—surprising observations reported on in the literature.

■ ASSOCIATED CONTENT

Supporting Information. Full reference 11. This material is available free of charge via the Internet at http://pubs.acs.org.

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