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Magnetoelectrochemistry of Gold Nanoparticle Quantized Capacitance Charging

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External magnetic fields may influence electrolyte mass transport or electron-transfer kinetics, or both.[1−3] For instance, it has been found that the electrochemical currents at a microelectrode for the reduction of nitrobenzene (NB) into radical anions ($NB^{\bullet -}$) increase with increasing magnetic field intensities and reach the maximum (minimum) when the electrode surface normal is perpendicular (parallel) to the magnetic fields.[1d,e] These observations were accounted for by the magnetohydrodynamic (MHD) flows resulting from magnetic field-driven convective transport of electrolyte species, where the Lorentz force ($\mathbf{F}_{MHD}$) acting on per unit volume of the solution is orientation-dependent (Scheme 1)

$$\mathbf{F}_{MHD} = \mathbf{J} \times \mathbf{B} \tag{1}$$

where **J** is the local flux of ions and **B** is the applied magnetic field. One can see that at $\mathbf{J} \parallel \mathbf{B}$, $\mathbf{F}_{MHD} = 0$, whereas at $\mathbf{J} \perp \mathbf{B}$, $\mathbf{F}_{MHD}$ reaches the maximum. Similar observations were also reported with other electrochemical systems.[1d] More importantly, in hydrogen fuel cell studies, it has been shown that the incorporation of magnetic microparticles (which provides a constant external magnetic field, though very weak) into the cell membranes leads to rather drastic enhancement of electrocatalytic currents.[2] However, thus far the molecular origin of these field-enhanced electrocatalytic activities remains largely unexplored. Several fundamental questions arise. Is it simply due to the mass transfer enhanced by magnetic fields? Or, more intriguingly, is it related to the field effects on electrode electron-transfer (ET) dynamics? An understanding of magnetic field effects on nanoscale electron transfer will be of fundamental significance in unraveling the mechanistic basis for the manipulations of these technologically crucial processes. Therefore, a magnetoelectrochemical study of nanosized particle molecules seems to be an appropriate starting point in addressing these issues.

It should be noted that thus far magnetoelectrochemistry has been mainly confined to simple conventional electroactive systems.[1] Most current interests are focused on the effects of magnetic fields on ion mass-transfer. In contrast, there has been no report on the magnetoelectrochemistry of nanoparticle molecules, to the best of our knowledge. In particular, there have been no systematic studies of the effects of magnetic fields on nanoparticle quantized charging chemistry in solutions. Studies of low-temperature solid-state physics of single-electron transistors (SETs, e.g., involving a single Al or Au particle)[4] have shown that the discrete electronic eigenstates of nanosized metal particles (through which electron tunneling occurs) can be manipulated by external magnetic fields. Additionally it is found that the experimental SET $I-V$ responses might be sensitive to the parity of the electron number in nanoparticle ground states.

These earlier results provide a fundamental framework for the studies of solution-phase nanoparticle magnetoelectrochemistry. Herein, using ultrasmall gold particles (diameter ≈ 1.6 nm) as the illustrating example,[5] we probe their discrete electronic energy states by exploiting their unique characters of quantized capacitance charging at ambient temperature.[6] Certainly, in electrochemical systems, we are measuring the collective contributions of particle ensembles in solutions, in contrast to the SET experiments[4] where a single particle is examined.

Scheme 1

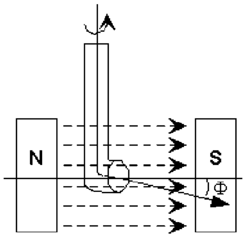

Figure 1 shows some representative cyclic (A, CVs) and differential pulse voltammograms (B, DPVs)[5] of *n*-decanethiolate-protected gold (C10Au) nanoparticles in a binary mixture of toluene and acetonitrile (2:1 v:v) with 0.10 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) at various magnetic intensities (shown as figure legends). In the absence of a magnetic field (solid line), one can see that there are four well-defined voltammetric peaks within the potential range of +0.6 to −1.2 V (vs Ag/AgCl) with a potential spacing of ca. 0.48 V. These voltammetric peaks are ascribed to the successive $1e^-$ chargings to the particle molecular capacitance, as observed previously.[6] However, upon the application of an external magnetic field, there are at least three features that warrant attention. First, the voltammetric currents of three of the four peaks increase (the other peak remains virtually invariant) with increasing magnetic field intensities. As these quantized charging processes are under diffusion control,[6] the observed increase of charging currents might be, in part, ascribed to the field-enhanced mass transfer of nanoparticle molecules. However, as these voltammetric responses were acquired at $\Phi = 180°$, contributions from the MHD effects can be excluded (eq 1). A similar observation was found in corrosion studies involving paramagnetic ions[7] where the voltammetric currents were found to increase with magnetic field intensity even at $\Phi = 180°$. This was interpreted on the basis of a gradient of magnetic susceptibility near the electrode surface (i.e., a concentration distribution of paramagnetic ions in solutions). Therefore, it is suspected that the present observation of the field-induced enhancement of particle charging currents (Figure 1) might be, at least partly, a result of the magnetoconvection of the particle molecules due to their paramagnetic properties. It has been shown that nanosized transition-metal nanoparticles exhibit nonzero magnetic moment (unpaired electrons),[4,8] which is attributable to the quantum confinement effect. Thus, the above hypothesis implies that the particle paramagnetic characters (electron parity) can be

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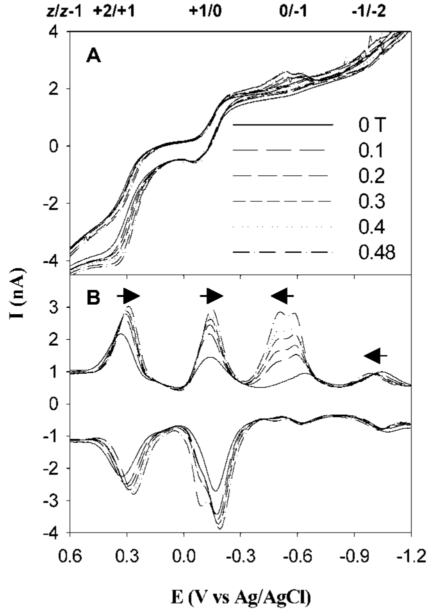

Figure 1. (A) CVs and (B) DPVs of 0.29 mM C10Au nanoparticles at a Pt microelectrode ($r = 25\ \mu$m) in 0.6 mL of toluene:acetonitrile (2:1, v:v) with 0.1 M TBAPF$_6$ at various magnetic field intensities (shown in figure legends) at $\Phi = 180°$. Potential scan rate in (A) 20 mV/s; in (B) pulse amplitude 50 mV; DC ramp 20 mV/s.

readily manipulated voltammetrically by their charge states, reflected in their different responses in a magnetic field (Figure 1).

Second, the formal potentials of these voltammetric peaks vary with the magnetic field intensities, where the shifts appear to be dictated by the particle charge states, that is, peaks of positive charge states shift cathodically, whereas those of negative charge states, anodically (indicated by the arrows in Figure 1). Additionally, the potential spacings (ΔV) between neighboring charging peaks decrease, and hence the nanoparticle (effective) molecular capacitances[5] ($C_{MPC} = e/\Delta V$ with e the electronic charge) increase, with increasing magnetic field intensities.

As the formal potentials reflect the reaction Gibbs energy in the corresponding single-electron transfers,[6b] these potential shifts seem to indicate that the particle electronic energy is varied by the external magnetic fields.

Third, the first negative peak in the cathodic scan and the first positive peak in the anodic scan (i.e., 0/±1 peaks, Figure 1; the potential of zero charge of gold nanoparticles, or PZC,[6] is typically found between −0.2 and −0.3 V) appear to be split into two subpeaks which become better-defined with increasing magnetic intensities. The potential spacing between these two subpeaks is ca. 78 mV. It was found previously[4] that, for nanosized particles, the mean spacing of independent electron spin-degenerate energy levels is

$$\Delta E \approx \frac{h^2}{2mk_F V} \tag{2}$$

where h is Planck's constant, m the electron mass, k_F the Fermi wave vector (1.20×10^8 cm^{-1} for Au[9]), and V the particle volume. This energy spacing can be manifested upon the interactions with an external magnetic field.[4] In the present case, the particle core diameter is about 1.6 nm.[5] Thus, we can estimate that the corresponding ΔE is about 59 meV. This is in a rather good agreement with the experimental value observed above (Figure 1). This splitting is only observed at the 0/±1 peaks and sensitive to the potential scanning directions, and an immediate consequence of this is that these two peaks now behave less reversibly. This suggests that external magnetic fields might influence the nanoparticle ET kinetics by changing the electronic energy structures, as it has been found previously that in low-temperature physics studies the first tunneling step is the rate-determining step in nanoscale electron-tunneling processes, which is sensitive to applied magnetic fields.[4] Additionally, it is likely that this field-induced splitting of the originally degenerate energy states might also play a role in the observed shifts of formal potentials and the variation of nanoparticle electron-transfer kinetics which become specific to the particle charge states, as suspected above.

In summary, this study suggests that the nanoparticle solution electrochemistry is manipulated by an external magnetic field, probably due to the intrinsic paramagnetic properties (electron parity) of the nanosized particle molecules that are contingent upon their charge states. Voltammetric responses imply that the nanoparticle electronic energy structure might be varied by the magnetic field. While the details of this unprecedented phenomenon remain to be explored, these observations do indicate that by using a relatively small magnetic field, one can probe the charge-transfer chemistry of nanosized particle molecules in a novel perspective. More detailed and systematic studies are currently underway to provide more insight into the unique properties of nanoscale electronic energy states and their associated electron-transfer chemistry.

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Supporting Information Available: Details of experimental procedure and the figure of the variation of nanoparticle effective capacitance with magnetic field intensity (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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