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Magnetoelectrochemistry of Nitrothiophenolate-Functionalized Gold Nanoparticles

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The electrochemical behaviors of *n*-decanethiolate-protected gold (C10Au) nanoparticles that had been exchanged with *p*-nitrothiophenolate (NTP) ligands at varied feed ratios were investigated in an external magnetic field (0–0.5 T). It was found that the NTP voltammetric currents are dependent on the electrode orientation and the intensity of the magnetic field. When the concentration of NTP in the particle is low (e.g., 10 or 30% exchange ratio), the currents at angles of 0 and 180° are greater than those at 90 and 270°. However, when the initial feed ratio is increased to 50%, the currents at angles of 0 and 180° are smaller than those at 90 and 270°. While these observed phenomena are ascribed to the magnetic field effects on nanoparticle mass transfer, their mechanistic origins are different. The former is attributable to the field-enhanced magnetoconvection due to the formation of an interfacial gradient of magnetic susceptibility (concentration), and the latter arises from magnetohydrodynamic interactions.

Introduction

Electrochemical processes can be easily manipulated by external magnetic fields. Most of the effects are related to the influence of the magnetic field on molecular transport. For instance, when a magnetic field is applied to a flux of ions (current), the ions will experience a Lorentz force that depends on the flux (**J**) and the magnetic field intensity (**B**) as well as the orientation of the flux relative to the magnetic field (namely, the so-called "right-hand" rule).[1–5] This is the well-known magnetohydrodynamic (MHD) phenomenon, that is,

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

Certainly one can see that this MHD effect will become more significant at higher fields as well as higher fluxes (concentrations). It also shows an interesting orientational dependence, where the force is maximum when $\mathbf{J} \perp \mathbf{B}$ and minimum when $\mathbf{J} \parallel \mathbf{B}$. Such effects on electrochemical redox reactions have been observed in a variety of systems. For instance, in the electroreduction of nitrobenzene (NB) at a microelectrode,[2] the voltammetric currents were found to reach the maximum (minimum) when the electrode

surface normal was perpendicular (parallel) to the magnetic field. The increase of voltammetric currents was ascribed to the enhancements of NB mass transfer that arose from the Lorentzian forces.

Other types of forces might also result from the magnetic field interactions. For instance, in a homogeneous field, the formation of a concentration gradient of molecules with unpaired electrons gives rise to a paramagnetic (PM) force[4]

$$\mathbf{F}_{PM} = \chi_m B^2 \nabla C / 2\mu_0 \tag{2}$$

where χ_m is the molar susceptibility, C is the concentration, and μ_0 is the vacuum permittivity. One can see that this force leads to the enhanced mass transfer of the PM molecules in the direction of increasing concentration, the so-called magnetoconvective effect.[5] This is in sharp contrast to the driving force from diffusion, which moves the electrolyte ions in the direction of decreasing concentration. Generally, the PM force is negligible compared to that from diffusion; however, for electrochemical processes involving electrolyte species with a significant magnetic susceptibility, it can become quite appreciable. In addition, one can see that the orientational dependences of the PM force and MHD effects are different, although both are reflected in the enhancement of the electrolyte ion mass transfer. More complicated behaviors are observed with nonuniform magnetic fields, which give rise to the so-called field-gradient forces.[2d–f,3,4]

Recently, we carried out a magnetoelectrochemical study[6] of nanoparticle quantized capacitance charging and observed current enhancement with the magnetic field intensity when the electrode surface normal is parallel to the magnetic field. It was interpreted on the basis of nanoparticle intrinsic magnetic properties (unpaired electrons) that could be varied by the particle charge states. It has been well-known that these nanosized particles can serve as nanoscale platforms for diverse chemical functionalizations by, for instance, exchange reactions,[7]

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(1) Fahidy, T. Z. J. *J. Appl. Electrochem.* **1983**, *13*, 553. (b) Tacken, R. A.; Janssen, L. J. J. *J. Appl. Electrochem.* **1995**, *25*, 1.
(2) Lee, J.; Gao, X.; Hardy, L. D. A.; White, H. S. *J. Electrochem. Soc.* **1995**, *142*, L90. (b) Ragsdale, S. R.; Lee, J.; Gao, X.; White, H. S. *J. Phys. Chem.* **1996**, *100*, 5913. (c) Grant, K. M.; Hemmert, J. W.; White, H. S. *J. Electroanal. Chem.* **2001**, *500*, 95. (d) Ragsdale, S. R.; Grant, K. M.; White, H. S. *J. Am. Chem. Soc.* **1998**, *120*, 13461. (e) Pullins, M. D.; Grant, K. M.; White, H. S. *J. Phys. Chem. B* **2001**, *105*, 8989. (f) Grant, K. M.; Hemmert, J. W.; White, H. S. *Electrochem. Comm.* **1999**, *1*, 319.
(3) Leventis, N.; Chen, M.; Gao, X.; Canalas, M.; Zhang, P. *J. Phys. Chem. B* **1998**, *102*, 3512. (b) Leventis, N.; Gao, X. *J. Am. Chem. Soc.* **2002**, *124*, 1079. (c) Leddy, J.; Minteer, S. D.; Gellett, W. L. *PCT Int. Appl.* **2001**, 48. (d) Leddy, J.; Chung, H. *Proc. Power Sources Conf.* **2000**, *39*, 144.
(4) Coey, J. M. D.; Hinds, G.; Lyons, M. E. G. *Europhys. Lett.* **1999**, *47*, 267. (b) Coey, J. M. D.; Hinds, G. *J. Alloys Compd.* **2001**, *326*, 238. (c) Hinds, G.; Coey, J. M. D.; Lyons, M. E. G. *Electrochem. Comm.* **2001**, *3*, 215.
(5) Waskaas, M.; Kharkatts, Y. I. *J. Phys. Chem. B* **1999**, *103*, 4876.

(6) Chen, S.; Yang, Y. *J. Am. Chem. Soc.* **2002**, *124*, 5280.
(7) Hostetler, M. J.; Templeton, A. C.; Murray, R. W. *Langmuir* **1999**, *15*, 3782. (b) Green, S. J.; Pietron, J. J.; Stokes, J. J.; Hostetler, M. J.; Vu, H.; Wuelfing, W. P.; Murray, R. W. *Langmuir* **1998**, *14*, 5612.

and the surface concentrations can be varied by the initial feed ratios of exchange ligands. Thus, one can envision that when magnetoelectrochemically active species are incorporated into the particle surface, the associated voltammetric responses will exhibit an orientational dependence that is a combined effect of the particle magnetic properties and the surface concentration of the electroactive moieties (and, hence, the faradaic flux).

In this paper, we describe a magnetoelectrochemical study of nitrothiophenol-functionalized gold (AuNTP) nanoparticles. The electrochemistry of AuNTP particles has been shown to be similar to that of NB monomers,[8] exhibiting two $1e^-$ reduction reactions in aprotic solvents. By varying the concentration of NTP on the Au nanoparticle surface, we observed a transition of the orientational sensitivity to an external magnetic field; namely, at high loadings, the voltammetric responses are consistent with the MHD phenomenon, whereas at low loadings, the PM contribution appears to be the dominating force in enhancing the nanoparticle mass transfer.

Experimental Section

Materials. Tetrabutylammonium hexafluorophosphate (TBAPF$_6$, Fluka) and *p*-nitrothiophenol (NTP, 95%, ACROS) were used as received. Solvents were acquired from typical commercial sources with the highest purity available. Water was supplied by a Barnstead Nanopure water system (>18 MΩ). The synthesis and fractionation of *n*-dodecanethiolate-protected gold (C10Au) particles have been described previously.[9] The particle core diameter is about 2 nm as determined by transmission electron microscopic measurements.

NTP-functionalized gold particles were obtained by place exchange reactions of the C10Au particles with calculated amounts of NTP. In a typical reaction, the particles and the NTP ligands were codissolved in dichloromethane under magnetic stirring for 2 days, where the initial feed ratio of NTP/C10S was varied from 10 to 75%. The solvent was then removed at reduced pressure, and the sample was rinsed thoroughly with methanol to remove excessive NTP and displaced C10S molecules. The resulting monolayer composition was then characterized by first I$_2$ desorption of the particle-protecting monolayers and then measurements of ^{1}H NMR spectra in CDCl$_3$ using a Varian 300 NMR spectrometer.

Electrochemistry. Electrochemical studies were carried out with a CHI 440 Electrochemical Workstation. A 90°-bent Pt disk microelectrode (radius, 25 μm) was used as the working electrode along with a Ag/AgCl electrode and a Pt coil as the (quasi) reference and the counter electrode, respectively. The Pt electrode was first polished with suspended 0.05-μm alumina slurries (Buehler) and sonicated in dilute HNO$_3$, H$_2$SO$_4$, and Nanopure water sequentially. It was then rinsed with acetone and dried in a gentle nitrogen stream prior to being introduced into the electrochemical cell for measurements. The electrolyte solutions were degassed with ultrahigh-purity nitrogen (99.999%, from Airgas) saturated with a binary mixture of toluene and acetonitrile (2:1 v/v) for at least 20 min prior to electrochemical measurements and blanketed with this N$_2$ atmosphere during the entire experimental procedure. A uniform magnetic field was created by using a GMW Electromagnet (3470) and varied by the applied currents (Power Ten, Inc.). The field intensity was measured with a direct current magnetometer (AlphaLab). The orientation of the field was defined by the angle between the unit surface normal, $\bar{n}$, and the magnetic field, **B**. The angle $\theta = 0°$ corresponds to the surface of the microdisk facing the south pole of the electromagnet. The experimental setup has been described previously.[2,6]

Results and Discussion

Exchange Reactions. As mentioned earlier, one of the intrinsic properties of nanosized alkanethiolate-

(8) Chen, S.; Huang, K. *Langmuir* **2001**, *17*, 2878.
(9) Brust, M.; Walker, M.; Bethell, D.; Schiffrin, D. J.; Whyman, R. *J. Chem. Soc., Chem. Comm.* **1994**, 801.

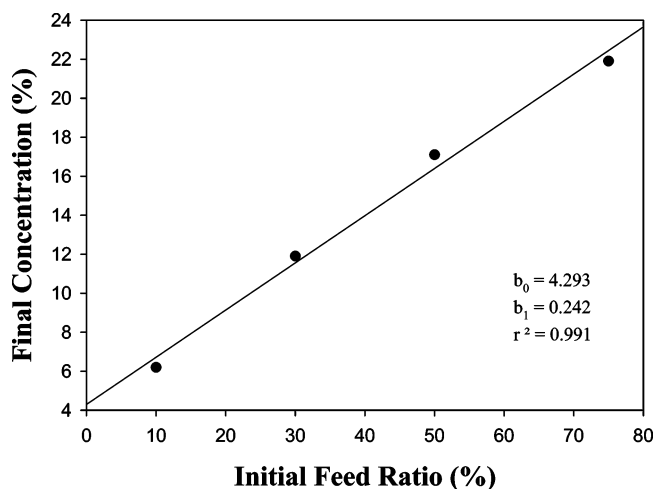**Figure 1.** Variation of the NTP concentration on the nanoparticle surface with initial feed ratios. Data obtained from NMR measurements after I$_2$ desorption of the protecting monolayers from the gold particle surface.

stabilized particles is that they can serve as nanoscale platforms on which further chemical functionalizations can be achieved by simple exchange reactions. These newly introduced functional moieties can then undergo more complicated chemical reactions, leading to the development of nanometer-sized multifunctional reagents. It has been found previously that the extent of the exchange reactions between alkanethiolate-protected nanoparticles and new thiol ligands is contingent upon the initial feed ratios as well as the reaction time, which is essentially a result of thermodynamic equilibrium between desorption of the original thiolates and adsorption of new thiol ligands.[7] The final concentration of the new ligands on the particle surface can then be assessed quantitatively by, for instance, NMR spectroscopy. This is one apparent advantage over two-dimensional self-assembled monolayers where conventional analytical tools are hard to apply.

Figure 1 shows the variation of the final NTP surface concentration with the initial feed ratio. Here, the initial feed ratio is defined as the molar ratio between the added NTP molecules and the *n*-decanethiolate (C10S) ligands of the particle-protecting layer, and the final concentration of NTP on the particle surface is defined as the fraction of the C10S ligands that are replaced by NTP molecules. This is calculated by integrating the peak areas of the aromatic protons and the terminal methyl protons in ^{1}H NMR spectra (not shown). From Figure 1, one can see that the incorporation of NTP into the particle surface increases linearly with the starting NTP concentrations. From the linear regression, about 24% of the initial NTP ligands are exchanged into the particle protecting layer. For straight-chain aliphatic counterparts, the extent of the exchange reactions in a comparable reaction time is about 50%; that is, 50% of the added new ligands will be incorporated into the particle-protecting shell.[7] This discrepancy most probably arises from the steric hindrance of the bulky aromatic ring in NTP molecules, as compared to the straight-chain counterparts.

From the transmission electron microscopy measurements, the particle core diameter is about 2 nm, corresponding to a Au$_{314}$ core configuration (by assuming a truncated octahedron model) with 91 C10S ligands on the core surface.[10] For the four exchange experiments shown here (10, 30, 50, and 75%), the final NTP surface
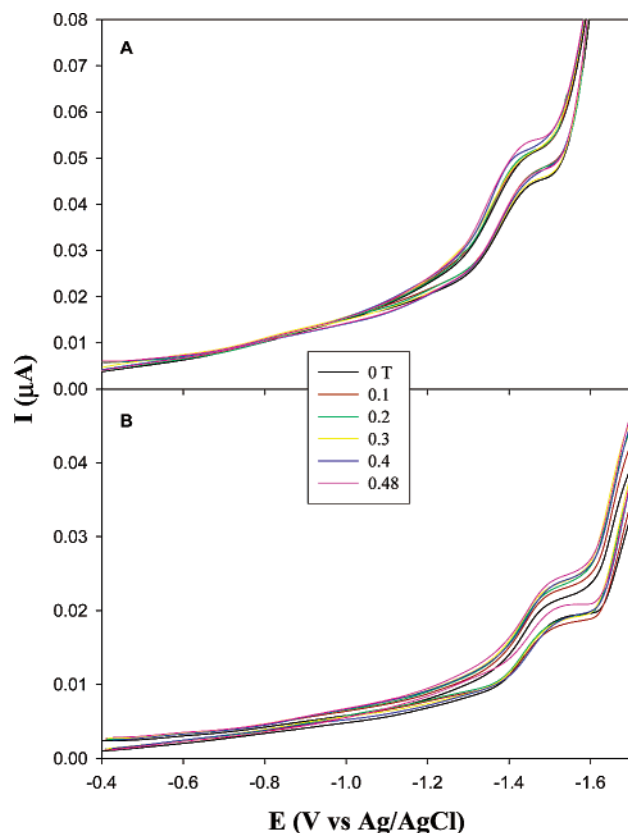
Figure 2. Representative CVs of C10Au nanoparticles with varied NTP loadings (A, AuNTP-III, 0.35 mM; B, AuNTP-II, 0.45 mM) at a Pt microelectrode (25 μm) in a binary mixture of toluene and acetonitrile (2:1 v/v) containing 0.1 M TBAPF$_6$. Magnetic field intensities are shown in the figure legend. The electrode orientation in part A is $\theta = 90°$ and in part B is $\theta = 180°$. The potential scan rate was 20 mV/s.

concentrations are 6.2, 11.9, 17.1, and 21.9%, respectively. That is, the final particle molecular compositions can be estimated as Au$_{314}$(C10S)$_{85}$NTP$_6$, Au$_{314}$(C10S)$_{80}$NTP$_{11}$, Au$_{314}$(C10S)$_{75}$NTP$_{16}$, and Au$_{314}$(C10S)$_{71}$NTP$_{20}$, respectively. The corresponding magnetoelectrochemical behaviors of the first three samples are reported next (because of solubility problems, we did not carry out electrochemical studies of the last sample). These are referred to as AuNTP-I, AuNTP-II, and AuNTP-III.

Magnetoelectrochemistry. Figure 2 shows some representative cyclic voltammograms (CVs) of the C10SAu particles with varied NTP loadings (A, AuNTP-III; B, AuNTP-II) in a binary mixture of toluene and acetonitrile with 0.1 M TBAPF$_6$ [particle concentrations (A) 0.35 mM and (B) 0.45 mM] under different magnetic field strengths. It should be noted that the electrode orientation in these two measurements is different: (A) $\theta = 90°$ and (B) $\theta = 180°$ (details below). First, one can see that in both cases there is a current step at about −1.4 V. This current step is ascribed to the first 1e$^-$ reduction of the nitrophenyl moieties that are attached to the particle surfaces. Due to the rapid spin of the particle molecules in solutions, all NTP moieties undergo redox reactions at the same thermodynamic potentials. In an earlier study,[8] we showed that in (dried) aprotic solvents, particle-bound nitrophenyl moieties exhibited similar electrochemical responses to those of NB monomers,[2] involving an anionic radical

(10) Hostetler, M. J.; Wingate, J. E.; Zhong, C.-J.; Harris, J. E.; Vachet, R. W.; Clark, M. R.; Londono, J. D.; Green, S. J.; Stokes, J. J.; Wignall, G. D.; Glish, D. L.; Porter, M. D.; Evans, N. D.; Murray, R. W. *Langmuir* **1998**, *14*, 17.
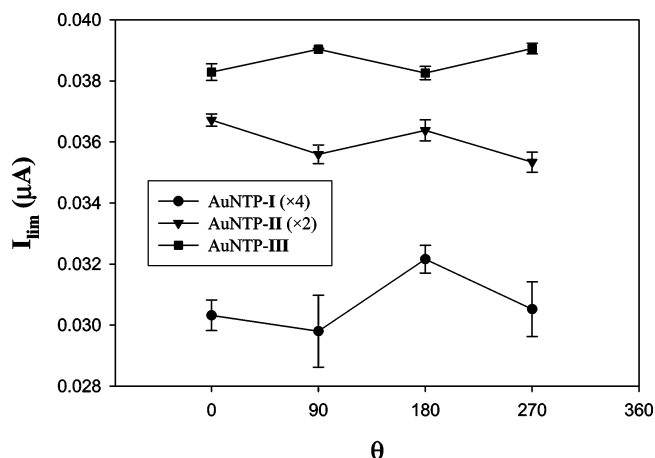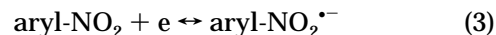

Figure 3. Variation of the NTP limiting currents with electrode orientations at varied NTP exchange ratios. The particle concentrations are AuNTP-I, 0.35 mM; AuNTP-II, 0.45 mM; and AuNTP-III, 0.35 mM. The potential scan rate was 20 mV/s. Lines are for eye-guiding only.

intermediate, and under mass-transfer control,

$$\text{aryl-NO}_2 + \text{e} \leftrightarrow \text{aryl-NO}_2^{\bullet -} \tag{3}$$

$$\text{aryl-NO}_2^{\bullet -} + \text{e} \leftrightarrow \text{aryl-NO}_2^{2-} \tag{4}$$

The voltammetric responses for AuNTP-I particles are similar to those for AuNTP-II, but with a slightly smaller current scale (not shown). Additionally, one can also observe that the current plateau is somewhat tilted, which is caused by the additional contribution to the voltammetric currents from charging to the nanoparticle molecular capacitance, as observed previously with ferrocene-functionalized gold particles.[7b]

Second, under the influence of an external magnetic field, the orientational effects are different, contingent upon the loadings of NTP on particle surfaces. Figure 3 shows the orientational effects of an external magnetic field on the limiting currents of these AuNTP particles (the error bars are from four independent measurements; the limiting currents are estimated by the same procedure as described previously).[7b] One can see that, for AuNTP-III particles, the limiting current for reaction 3 reaches the maximum when the electrode surface normal is perpendicular to the magnetic field lines (i.e., $\theta = 90$ and 270°) and the minimum when the electrode surface is facing the magnetic poles (i.e., $\theta = 0$ and 180°). This observation is similar to that observed in concentrated NB solutions[2] although significantly smaller due to the smaller currents associated with dilute solutions of the AuNTP particles. It can be interpreted on the basis of MHD effects, which enhance the nanoparticle (or NB) mass transfers. From eq 1, one can see that the Lorentzian force is maximized when **J** ⊥ **B** and is 0 when **J** ∥ **B**. Certainly one can see that the MHD effects will be more significant with a higher ion flux (i.e., electrolyte concentration and, hence, current).

However, when the initial feed ratios of NTP is lowered down to 30 and 10% (i.e., AuNTP-I and AuNTP-II particles), completely opposite orientational effects are found. In these two cases, the limiting currents at $\theta = 0$ and 180° are actually greater than those at 90 and 270°. Similar orientational effects were also observed in electrodeposition and electrochemical corrosion studies where PM ions were involved.[4,5] The phenomenon was interpreted on the basis of field-induced magnetoconvection

that arose from the formation of an interfacial gradient of magnetic susceptibility (concentration). One should note that, in the first $1e^-$ reaction of the NTP moieties, the product is a radical anion (eq 3) and a radical concentration gradient is formed at the electrode interface with the concentration decreasing from the electrode surface to the bulk solution. From eq 2, the PM gradient force tends to move a volume element containing PM species in the direction of increasing concentration. Consequently, it can be anticipated that the radical anions will be locally confined at the electrode interface, leading to the shrinking of the diffusion layer and, hence, enhancement of the voltammetric (faradaic) currents.

At $\theta = 90$ and $270°$, the Lorentz force (eq 1) arising from the ionic flux creates a stirring of the electrolyte solution. While it enhances the mass transfer of the ionic species (vide ante), it also helps the ionic species emanate from the interface to the bulk solution. Clearly, this latter effect offsets that of the PM force as discussed above. By contrast, at $\theta = 0$ and $180°$, the Lorentz force is minimum (eq 1) and the main driving force is from the PM effect. Therefore, one can see that the final orientational dependence of the voltammetric responses is determined collectively by the relative contributions (amplitudes) of these driving forces, which are manifested in the effects on nanoparticle mass transfer.

Coey et al.[4] gave a quite detailed account of the relative amplitudes of varied forces that electrolyte ions experienced in solutions. For typical electrolyte ions, the PM force is about 5 orders of magnitude smaller than the diffusion force and, thus, is generally negligible. However, these comparisons are based on an assumption that the magnetic susceptibility[4] (χ_m) of the electrolyte ions is on the order of 10^{-8}. For PM materials, the magnetic susceptibility[11] is typically found within the range of 10^{-3}–10^{-5}, where the PM force becomes more comparable to diffusion contributions. In addition, in our previous studies of nanoparticle magnetoelectrochemistry,[6] we found that the nanosized gold particles might also exhibit PM or diamagnetic properties depending upon the particle charge states. The combination of these two contributing factors leads to a more appreciable force due to the PM properties of the NTP-functionalized particles, especially at lower loadings of NTP on nanoparticles, where the faradaic current is smaller (and, hence, smaller Lorentz force).

Third, from Figure 2, one can see that, at these different orientation angles, the voltammetric currents increase with increasing magnetic field strength, as expected from eqs 1 and 2. Figure 4 shows the effects of external magnetic field strength on the limiting currents of NTP moieties attached to the C10SAu particle surfaces. One can see that there appears to be a linear increase of the limiting currents with the magnetic field intensities.[12] These observations indicate that PM effects can be detectable
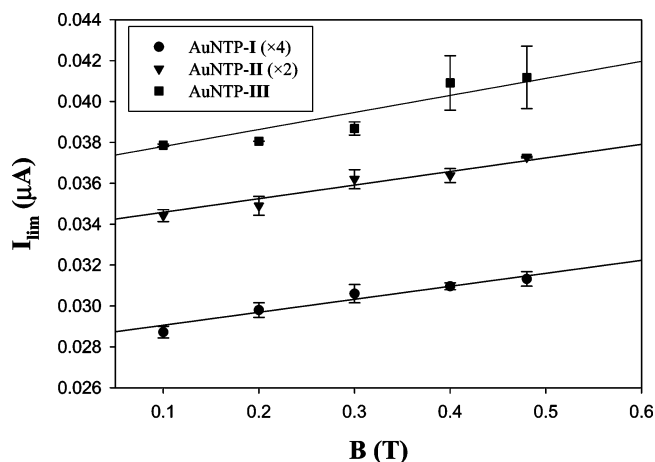

Figure 4. Variation of the NTP limiting currents with the magnetic field intensity at varied NTP exchange ratios. The experimental conditions are the same as those in Figure 3. Symbols are experimental data while lines are linear regressions.

even in very low magnetic fields, whereas MHD interactions are more appreciable in higher fields and more concentrated electrolyte solutions.[2,3]

Conclusion

The above study demonstrates that the effects of external magnetic fields on nanoparticle mass transfer may be governed by two competing mechanisms, one from the conventional MHD effects and the other arising from the PM properties of the particle molecules. While MHD effects show a sensitive dependency of nanoparticle mass transfer on the electrode orientation relative to the magnetic field, the end result of the PM force always tends to move a volume element containing PM species in the direction of increasing concentration. The combination of two mechanisms leads to an interesting orientational discrepancy of the particle mass transfer that depends on the specific molecular structure. At high NTP loadings, the voltammetric current from the faradaic reactions of the NTP moieties reaches the maximum (minimum) when the electrode surface normal is perpendicular (parallel) to the magnetic field lines. By contrast, at a lower NTP loading, the maximum (minimum) currents are observed at $\theta = 0$ and $180°$ (90 and $270°$). Because the MHD force is proportional to the flux of the electrolyte ions, it becomes more dominant at higher concentrations of the NTP moieties (and, hence, greater faradaic currents), whereas at lower concentrations, the PM force becomes more comparable, leading to the orientational manipulation of the NTP voltammetric responses.

(11) Kittel, C. *Introduction to Solid State Physics*, 5th ed.; John Wiley & Sons: New York, 1976; p 154.
(12) We did not observe a $I_{lim} \propto B^2$ relationship for AuNTP-I and AuNTP-II particles, as anticipated from eq 2. This might be accounted for by at least two possible sources: (a) the small range of the magnetic field strength employed in this study and (b) combined effects with the MHD force.