Magnetic control – switchable ultra-high magnetic gradients at Fe_3O_4 nanoparticles to enhance solution-phase mass transport

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The ultra-high magnetic gradients at Fe_3O_4 nanoparticle modified electrodes (>10^8 T/m) induce enhanced mass transport to electrodes. This is attributed to the magnetic field gradient force and the superparamagnetic properties of nano-Fe_3O_4 enabling switching of the force using an external magnetic field.

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ABSTRACT

Enhancing the mass transport to electrodes is desired in almost all fields of electrochemical sensing, electrocatalysis and energy storage or conversion. Here, a method is presented that allows doing so by means of the magnetic gradient force generated at magnetic nanoparticle modified electrodes. It is shown using Fe_3O_4 nanoparticle modified electrodes that the ultra-high magnetic gradients (>10^8 T/m) established at the magnetized Fe_3O_4 nanoparticles speed up the transport of reactants and products at the electrode surface. Using the Fe(III)/Fe(II)-hexacyanoferrate redox couple, it is demonstrated that this mass transport enhancement can conveniently and repeatedly be switched on and off by the application and removal of an external magnetic field, thanks to the superparamagnetic properties of magnetite nanoparticles. Thus, it is shown for the first time that magnetic nanoparticles can be utilized to control mass transport in electrochemical systems. Importantly, this approach avoids the implementation of any means of mechanical agitation and is therefore particularly interesting for application in micro- and nanofluidic systems and devices

1 Introduction

Numerous studies report the beneficial application of magnetic nanoparticle modified electrodes to enhance the performance of electrochemical sensors and devices, ranging from the detection of biomolecules [1-4] to energy conversion [5-7]. At the same time, tremendous effort has been made to increase and actively control mass transport of reactants to electrodes, for instance using flow cells [8-10], rotating disc electrodes [11, 12], insonation [13, 14] or magnetic fields [15-18]. Herein the combination of both these aspects is demonstrated for the first time: the use of magnetic fields generated by magnetic

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nanoparticles to locally enhance the mass transport to electrodes and thus promote electrochemical processes. As a proof-of-concept one of the most widely used redox couples, $[Fe(CN)_6]^{4-}$/ $[Fe(CN)_6]^{3-}$ is demonstrated to show increased currents at electrodes modified with magnetized magnetite nanoparticles (Fe_3O_4 NPs) of 8±2 nm in diameter. Geometric and magnetic field effects on mass transport are delineated by direct comparison of the chronoamperometric response of these electrodes with electrodes modified with diamagnetic gold and silver nanoparticles in the presence and the absence of the magnetic field generated by a standard commercial permanent magnet. It is found that the strong magnetic field gradients generated by Fe_3O_4 nanoparticles cause a four times larger increase in the electrochemical current than caused by the low-gradient magnetic field supplied by the permanent magnet at Au or Ag nanoparticle modified electrodes. This observation is related to the two relevant magnetic forces: the Lorentz force and the magnetic field gradient force. The potential of the latter to non-invasively enhance the local mass transport at electrodes by means of magnetic nanoparticle modification is highlighted and the relevant parameters are discussed. It is further demonstrated that the superparamagnetic properties of Fe_3O_4 NPs allow to repeatedly switch this magnetic field induced convection on and off by the application and removal of the external magnet.

2 Theory - magnetic field effects in electrochemistry

In contrast to gas phase reactions, in liquids the conversion of reactants at a reactive surface is greatly limited by the slow diffusion of both reactants and products to or away from this surface. Thus, in electrochemistry reducing the diffusion layer thickness, the distance reactants have to diffuse to reach an electrode, by forcing a convective flow is advantageous. One convenient option to do so while avoiding mechanically moving parts is the application of magnetic fields [16, 19, 20].

The classical magneto-hydrodynamic effect (MHD-effect) [21] refers to a Lorentz force ($\mathbf{f}_L$) driven convection of the electrolyte, where $\mathbf{f}_L$ results as the cross product of the current density $\mathbf{j}$, in the presence of an external magnetic field of magnetic induction $\mathbf{B}$:

(1)

While this force dominates in homogeneous and low-gradient magnetic fields, in the presences of high magnetic field gradients, the magnetic field gradient force, or Kelvin force $\mathbf{f}_m$, has to be considered additionally [22, 23]:

; (2)

where μ_0 denotes the permeability of free space ($4\pi\times10^{7}$ A m), $\nabla\mathbf{B}$ the gradient of the magnetic induction and the magnetic susceptibility of the solution χ_{sol} is the sum of the molar magnetic susceptibilities χ_{mol} of all electrolyte components i weighted by their concentration c_i:

(3)

In systems undergoing electrochemical reactions χ_{sol} changes dramatically near the electrode when concentration gradients of paramagnetic species are established, for instance due to their generation or consumption at an electrode. In these cases, the magnitude of the magnetic field gradient force changes strongly across the diffusion layer and – provided suitably high magnetic field gradients in the same region, a convective flow may be induced in the direct vicinity of the electrode. Accordingly, the influence of $\mathbf{f}_m$ on the convective mass transport in electrochemical systems can be described by eq. (4); a derivation of which is provided in the SI and discussed in detail in [23-27].

(4)

where $\chi_{mol,para}$ and c_{para} are the molar magnetic susceptibilities and concentration of paramagnetic species.

According to Mutschke et al. [23], which of the two magnetic forces dominates the electrochemical response in a particular system can be estimated via the ratio of the dimensionless parameters R_{VB} and R_{MHD} rationalizing the magnetic field gradient and the Lorentz force in terms of the length scale they act on:

; (5)

where z is the number of electrons exchanged per reacting species and D its diffusion coefficient, F is the Faraday constant (96,485 C mol^{-1}), δ is the diffusion layer thickness and L the specific length scale of the magnet(s) applied. According to that, the smaller the applied magnet is, the more dominant the magnetic field gradient force should be.

The enhancement of electrochemical processes by magnetic field induced convection has to date been limited to magnetic features with at least one of their dimensions being of macro- and microscopic length [15, 28-31]. Herein, significant effects are evidenced for the first time using magnetic nanoparticles. Besides allowing the local application of very large magnetic field gradients, the use of magnetic nanoparticles is also preferable as techniques for both their large scale production and surface immobilization exist, a pre-requisite for their application in real-world devices. When superparamagnetic nanoparticles are applied, such as the Fe_3O_4 NPs used herein, the magnetic field gradient can not only be applied in the spatial, but also in the temporal domain, as it can be turned on and off by virtue of an external magnetic field being superimposed or not.

3 Experimental

3.1 Chemical reagents and instrumentation

Potassium hexacyanoferrate (III), 98+% (Lancaster), potassium hexacyanoferrate (II) trihydrate, 99% (Lancaster) and potassium nitrate (Sigma-Aldrich) were used as received, without further purification. Hydrochloric acid (Sigma-Aldrich, >37%) was diluted to the concentration of 0.1 M. All solutions were prepared using deionised water (Millipore) with a resistivity of 18.2 MΩ cm at 25 °C.

Electrochemical experiments were performed in a thermostated (25.0±0.2 °C) Faraday cage, using a μAutolab Type III potentiostat (Utrecht, Netherlands). All measurements were conducted using a standard three electrode setup utilising a carbon rod counter electrode (3 mm diameter) and a saturated calomel reference electrode (SCE, BASi, West Lafayette, IN, USA). A bare or modified glassy carbon electrode (GCE, 3 mm diameter) was employed as a working electrode (WE).

The three electrodes were set up in a cylindrical PEEK cell (3 cm diameter). In experiments involving the application of a magnet, this cell was placed in front of the centre of a rectangular 50×50×25 mm^3 NdFeB permanent magnet (45 MG Oe, Bunting Magnetics Europe Ltd., UK) with a glassy carbon working electrode at the centre of the cell (1.5 cm away from the NdFeB magnet surface). The magnetic field strength generated by the NdFeB magnet at this distance is ca. 1.6×10^5 A m^{-1} as simulated by the numerical 3D magnetostatic field solver Amperes 9.0 (Enginia Research Inc.); see SI for details. This value of field strength is large enough to magnetize Fe_3O_4 NPs as reported in [32, 33]. The counter electrode (CE) was positioned opposite the WE and the reference electrode (RE) in close vicinity to the WE (see Fig. 1) to minimize potential drop in the system.

Figure 1 Electrochemical cell setup; RE = SCE reference electrode, WE = glassy carbon working electrode, CE = carbon rod counter electrode and electrolyte = 9.5 mM hexacyanoferrate (II) or 9.5 mM hexacyanoferrate (III) with 0.50 M KNO_3 supporting electrolyte

3.2 Syntheses and characterization of nanoparticles

3.2.1 Syntheses

Citrate-capped Au NPs were provided by Mintek (Randburg, South Africa). Citrate-capped Ag NPs were synthesized using the method developed by Wan et al. [34].

Citrate-capped Fe_3O_4 NPs were synthesized according to the method reported by Williams et al. [35] by dissolving 10 mmol iron (II) chloride tetrahydrate ($FeCl_2{\cdot}4H_2O$, Sigma-Aldrich) and 20 mmol iron (III) chloride hexahydrate ($FeCl_3{\cdot}6H_2O$, Sigma-Aldrich) in 27 mL solution of 0.8 M hydrochloric acid (HCl, Sigma-Aldrich). Then 250 mL of a 1.7 M aqueous solution of sodium hydroxide (NaOH) was added and the mixture is stirred at room temperature for 30 min to allow for the co-precipitation of Fe_3O_4 nanoparticles (NPs). A NdFeB permanent magnet was then used to separate the resulting Fe_3O_4 NPs from the reaction mixture. The next step differs from that reported by Williams et al. [35] since we sought to introduce citrate as a capping agent of the NPs to prevent oxidation of Fe_3O_4 in the presence of oxygen in air. This was done by adding 3.5 g of sodium citrate tribasic dehydrate (Sigma-Aldrich) to the suspension of 3.3 g of Fe_3O_4 NPs in 135 mL H_2O, heating it to 100 °C for 30 min with constant stirring and leaving it to cool to room temperature afterwards. The final citrate-capped Fe_3O_4 NPs products were washed with deionised water, separated from the reaction mixture using a NdFeB permanent magnet and re-dispersed in H_2O with the NP concentration of 3.5 g L^{-1}.

3.2.2 Characterization

Citrate-capped Au NPs were characterised via SEM imaging using a Leo Gemini II Field emission gun microscope (Zeiss, Germany). The analysis of the SEM images with ImageJ software (1.47, National Institutes of Health, USA) yielded mean radii of 12.9±3.5 nm (see Fig. 2a and 2b).

Citrate-capped Ag NPs and citrate-capped Fe_3O_4 NPs were characterised by TEM imaging using an FEI TECNAI T20 and analysed with ImageJ software to be 3.4±2.2 nm (see Fig. 2c and 2d) and 4.0±1.0 nm in radii (see Fig. 2e and 2f) respectively.

Additional nanoparticle characterization data can be found in the Supplementary Material, providing additional nanoparticle sizing data and compositional analysis of the Fe_3O_4 nanoparticles.

Figure 2 a) SEM image of Au NPs, **b)** Au NPs size distribution from ImageJ analysis, **c)** TEM image of Ag NPs, **d)** Ag NPs size distribution from ImageJ analysis, **e)** TEM image of Fe_3O_4 NPs and **f)** Fe_3O_4 NPs size distribution from ImageJ analysis

3.3 Experimental Procedures

3.3.1 Modification of GC electrodes with NPs

Prior to use, glassy carbon macroelectrodes were polished using 1.0, 0.3 and 0.05 μm alumina powder (Buehler) on soft lapping pads (Buehler), then sonicated in deionised water in an ultrasonic bath for 1 minute to remove any adsorbed material. The glassy carbon macroelectrodes were then modified by dropping 2 μL of nanoparticles suspension onto the surface and letting the electrode dry under nitrogen flow gas.

3.3.2 Electrochemical Stripping Experiment: Linear Sweep Voltammetry

To quantify the amount of NPs immobilized on the surface of the electrode, electrochemical stripping experiments in 0.1 M HCl solution were performed [36]. The technique allows us to electrochemically reduce or oxidise the NPs and hence quantify the number of NPs undergoing the process. Consequently, the electrode surface coverage can be deduced. Accordingly, the NPs modified glassy carbon electrodes were subjected to linear sweep voltammetry at the scan rate of 0.01 V s^{-1} over a potential range of E = 0 – 1.15 V, E = 0 – 0.8 V and E = 0.5 – (-0.5) V vs. SCE for Au, Ag and Fe_3O_4 NPs respectively [37-39].

3.3.3 Cyclic Voltammetry

The redox systems of 9.5 mM $[Fe(CN)_6]^{4-}$ (aq) or 9.5 mM $[Fe(CN)_6]^{3-}$ (aq) solutions fully supported with 0.50 M KNO_3 (aq) were used to study the effect of mass transport enhancement when the working electrode was modified with magnetic NPs.

The redox species were first subjected to cyclic voltammetry in the absence of a magnetic field to measure the values of the formal and peak potentials, and provide a guide for the overpotential required in chronoamperometric measurements. Cyclic voltammetry was performed at a scan rate of 0.1 V s^{-1} in the potential window of -0.15 V to 0.60 V vs. SCE.

3.3.4 Chronoamperometry

Chronoamperometry was chosen to study mass transport in electrolyte solution since a sufficiently high overpotential can be applied so all the redox species of interest which reaches the electrode is immediately consumed. The chronoamperometric currents are therefore controlled by mass transport alone which in this case arises from diffusion and magnetic field-induced forced convection. Migration is negligible in the presence of excess supporting inert electrolyte (0.50 M KNO_3). Natural convection due to a temperature gradient is excluded by

thermostating the electrochemical cell and natural convection due to density gradients can be neglected for the short experimental times of no longer than 10 s for the electrochemical system considered (9.5 mM $[Fe(CN)_6]^{3-/4-}$ (aq)) as described elsewhere [40, 41].

The comparison of currents at 10 s in the presence and absence of the magnetic fields is therefore indicative of the effect of magnetic field on mass transport. For the systems of $[Fe(CN)_6]^{4-}$ (aq) and $[Fe(CN)_6]^{3-}$ (aq), the potentials of 0.35 V and 0.06 V were applied respectively.

Repeated application and removal of the external rectangular 50×50×25 mm^3 NdFeB permanent magnet (45 MG Oe) were used to turn 'on' and 'off' the magnetic field effects ($\mathbf{f}_L$ and $\mathbf{f}_m$). The same modified electrode was used in the presence and absence the magnetic field. This was to ensure the surface geometry of the electrode was the same throughout each experiment, allowing direct probing of the magnetic field effects under identical NPs coverage and their arrangement on the electrode surface.

The chemical stability and adhesion of Fe_3O_4 NPs throughout each set of experiments was evidenced by electrochemical stripping of the surface immobilized Fe_3O_4 NPs from the GC electrode in 0.1 M HCl either directly after the electrode modification or after subjecting them to at least five chronoamperometric measurements in the presence and absence of a magnetic field. In both cases the characteristic reductive stripping peak at 0.1 V vs SCE confirmed the presence of Fe_3O_4 NPs on the electrode surface. A small peak at -0.1 V vs SCE was also observed, showing the presence of ca. 6% of Fe_2O_3 in both cases and thus confirming the chemical stability of the nanoparticles during the magneto-electrochemical studies.

4 Results and discussion

4.1 Results

First, experiments utilising diamagnetic Au or Ag NP modified electrodes were performed in comparison with bare electrodes. This delineates the effects of NP modification of electrodes such as the change in electrode geometries from the magnetic contribution arising from the 'quasi-homogeneous' fields (with low magnetic gradients) generated from an external NdFeB permanent magnet ($\mathbf{f}_L$).

Next, Fe_3O_4 NP modified electrodes were employed. Due to the high magnetic field gradients generated at the surface of the NPs, both $\mathbf{f}_L$ and $\mathbf{f}_m$ act in this case. By comparing the results obtained in this case to that of the diamagnetic NP modified electrodes (the low-gradient $\mathbf{f}_L$-only case), the contributions of $\mathbf{f}_L$ and $\mathbf{f}_m$ can be separated.

4.1.1 NP-modified electrodes – surface coverage

In order to compare the effect on mass transport when the working electrodes were modified with different NPs, either the electrode surface coverage (θ, see eq. (6)) or the amount (moles) of NPs immobilized on the surface (n) can be used as a fixed parameter (see Fig. 3). Since the sizes and densities of the different NPs used were different, it was not possible to fix both of these parameters (θ and n) at the same time. Both parameters were studied separately.

Surface coverages (θ) are calculated as the fractions of electrode surface area covered with NPs:

(6)

where N_{NP} is the number of NPs (moles) on the surface calculated according to [42], r_{NP} is the radius of a NP and r_e is the radius of a disc GC electrode.

As the concentrations and sizes of the NPs in each suspension are known (Au: 0.05 g L^{-1}, Ag: 0.1 g L^{-1} and Fe_3O_4: 3.5 g L^{-1}), 2 μL of each is expected to give approximately 50-60% surface coverage (θ) for Ag and Fe_3O_4 or the number of NPs immobilized on electrode surface (n) of 4-5×10^{-10} moles for Au and Fe_3O_4. This was confirmed by electrochemical stripping experiments in 0.1 M HCl solution. The resulting stripping voltammograms are shown in Fig. 4.

Electrochemical stripping of the thus surface immobilized NPs from the GCE gave the stripping charges of 80±17 μC, 180±27 μC and 96±15 μC for Au, Ag and Fe_3O_4 NPs respectively.

Figure 3 Glassy carbon working electrodes modified with (**top right**): Au NPs with the same amount of NPs immobilized on the surface (n) as for the Fe_3O_4 NPs and (**bottom right**): Ag NPs with the same electrode surface coverage (θ) as for the Fe_3O_4 NPs

The total charges (Q) obtained from linear sweep voltammetry are given by eq. (7):

(7)

where n denotes the amount of particles (moles) undergoing electrochemical processes, z is the number of electrons exchange per formula unit and F is the Faraday constant. The number of electrons exchanged per formula unit (z) are 1.9 for the oxidation of Au [43], 1 for the oxidation of Ag [44] and 2 for the reduction of Fe_3O_4 [37, 39, 45].

For Au and Fe_3O_4 NPs, these charges corresponded to 4.4±0.9 ×10^{-10} moles and 5.0±0.8 ×10^{-10} moles of particles immobilized on the electrode surface respectively.

While for Ag and Fe_3O_4 NPs, the electrode surface coverages calculated from the stripping charges according to eq. (6) were found to be 60±9% and 61±9% respectively. More details on the calculation of surface coverages are given in the SI.

4.1.2 Cyclic voltammetry of the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple

For bare electrodes, cyclic voltammetry (CV) at a scan rate of 0.1 V s^{-1} was studied for the oxidation of $[Fe(CN)_6]^{4-}$ and reduction of $[Fe(CN)_6]^{3-}$ in fully supported (0.50 M KNO_3) aqueous electrolyte in the absence of a magnetic field. The peak potentials for the oxidation and reduction processes were observed at 0.26 V and 0.16 V vs. SCE respectively (see Fig. 5).

Figure 4 Linear sweep voltammograms of the electrochemical stripping of NPs supported on GC electrodes in 0.1 M HCl, $dE/dt = 0.01$ V s^{-1}

Accordingly, potentials significantly higher than 0.26 V and lower than 0.16 V vs. SCE were considered as large enough to overcome kinetic limitations in the oxidation of $[Fe(CN)_6]^{4-}$ and reduction of $[Fe(CN)_6]^{3-}$ respectively; allowing the study of mass transport in chronoamperometry.

For Fe_3O_4 NP-modified electrodes, the CV was first run in 0.50 M KNO_3 electrolyte, without the redox active $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_6]^{3-}$ species. No peak was observed, indicating that Fe_3O_4 NPs were chemically and electrochemically stable in this medium in the potential range of -0.15 V to 0.60 V vs. SCE. Cyclic voltammetry of the oxidation of $[Fe(CN)_6]^{4-}$ and reduction of $[Fe(CN)_6]^{3-}$ in fully supported (0.50 M KNO_3) aqueous electrolyte in the absence of a magnetic field was also done using the Fe_3O_4 NP-modified electrodes. Similar CVs as for the bare electrodes were observed.

Figure 5 CVs of 9.5 mM $[Fe(CN)_6]^{4-}$ aqueous solution (blue) and 9.5 mM $[Fe(CN)_6]^{3-}$ aqueous solution (brown), fully supported with 0.5 M KNO_3 (aq), $dE/dt = 0.1$ V s^{-1}

4.1.3 Chronoamperometry

The effects of the magnetic field on the mass transport were studied by running chronoamperometric measurements for 10 s in the presence and absence of an external NdFeB permanent magnet.

Figure 6 chronoamperograms of 9.5 mM $[Fe(CN)_6]^{4-}$ (aq) and 9.5 mM $[Fe(CN)_6]^{3-}$ (aq) in the presence (red) and in the absence of a magnetic field (black)

First, the effects of 'low gradient' magnetic fields ($\mathbf{f}_L$-only case) were studied using bare WE and WE modified with diamagnetic Au or Ag NPs. Second, additional effects from 'high gradient' magnetic fields ($\mathbf{f}_L + \mathbf{f}_m$) created by modification of the WE with superparamagnetic Fe_3O_4 NPs were investigated.

Potentials of 0.35 V and 0.06 V vs. SCE were chosen for chronoamperometric studies of 9.5 mM $[Fe(CN)_6]^{4-}$ and 9.5 mM $[Fe(CN)_6]^{3-}$ aqueous solutions respectively to ensure that the systems were under mass transport control. Chronoamperograms for the oxidation of 9.5 mM $[Fe(CN)_6]^{4-}$ aqueous solution and the reduction of 9.5 mM $[Fe(CN)_6]^{3-}$ aqueous solution in the presence and absence of a magnetic field are shown in Fig. 6 for bare electrodes and electrodes modified with diamagnetic NPs (Au and Ag) and in Fig. 7 for Fe_3O_4 NP-modified electrodes.

Figure 7 chronoamperograms of **a)** 9.5 mM $[Fe(CN)_6]^{4-}$ (aq) solution, **b)** 9.5 mM $[Fe(CN)_6]^{3-}$ (aq) solution in the presence of magnet (red) and in the absence of magnet (black)

The currents and charges observed for the oxidation of $[Fe(CN)_6]^{4-}$ and reduction of $[Fe(CN)_6]^{3-}$ in fully supported (0.5 M KNO_3) aqueous electrolytes in the absence of a magnetic field are summarized in Table 1 and 2 respectively.

The time-dependent currents (I) and the current integrals over time (charges, Q) were used to quantify the magnetic field effect on mass transport.

The current enhancement (γ_I) was quantified using the following expression:

(8)

where I_B and I_0 are the currents measured at the same experimental times in the presence and absence of an external NdFeB magnet respectively.

Similarly, the charge enhancement (γ_Q) was calculated by

(9)

where Q_B and Q_0 are the total charges measured at the same experimental timescale in the presence and absence of an external NdFeB magnet respectively.

It was found that when a bare glassy carbon electrode was employed as the working electrode, the current and charge enhancement was no greater than ca. 2% for both the oxidation of $[Fe(CN)_6]^{4-}$ and the reduction of $[Fe(CN)_6]^{3-}$ (see Fig. 6).

When a glassy carbon electrode modified with diamagnetic NPs (Au or Ag NPs) was used, the limiting currents and current integrals increased by no greater than ca. 2% in the presence of magnet for both the oxidation of $[Fe(CN)_6]^{4-}$ and the reduction of $[Fe(CN)_6]^{3-}$ (see Fig. 6). The γ_I and γ_Q values show

that there was no significant difference from the bare electrode, and therefore modification of electrodes with diamagnetic NPs was demonstrated as having no effect in the current and charge enhancement of electrochemical processes.

For Fe_3O_4-modified glassy carbon electrode, ~8 % increase in currents and charges were observed for both $[Fe(CN)_6]^{4-}$ and $[Fe(CN)_6]^{3-}$ systems (see Fig. 7 for chronoamperograms). Note that upon the removal of the external NdFeB magnet, the chronoamperometric currents return to their initial values before the first placement of the magnet as shown in Fig. 8 for the oxidation of 9.5 mM $[Fe(CN)_6]^{4-}$.

Figure 8 Chronoamperograms of the oxidation of 9.5 mM $[Fe(CN)_6]^{4-}$ (aq) solution utilising the Fe_3O_4-modified glassy carbon electrode with an external NdFeB magnet acting as a switch turning 'on' and 'off' the magnetic fields

4.2 Discussion

The magnetic fields applied in the bare electrodes and electrodes modified with diamagnetic NPs systems were quasi-homogeneous; that is the magnetic field gradients were small ($\nabla\mathbf{B} \sim 1\times10^{1}$ T m^{-1}, see SI for details) and hence insignificant. The small current and charge enhancements observed for these systems can thus be attributed to the Lorentz force ($\mathbf{f}_L$, see eq. (1)) driven magnetohydrodynamic effect (MHD) which has been previously reported in many systems [21, 27, 46-48].

On the contrary, significantly greater current enhancements were observed for the Fe_3O_4-modified electrodes compared to those obtained from diamagnetic NP modified electrodes. This is the result of large magnetic gradient forces due to the high magnetic gradients created at magnetic Fe_3O_4 NPs in addition to the Lorentz force from the external NdFeB magnet.

The effects of magnetic gradient force have been previously reported for macro- and microscopic magnetic features [22, 23, 26, 31, 49-54]. For the electrochemical set-up presented in this paper (a closed cell), the potential (irrotational) part of the force would "press" against the wall and hence have no effect on electrolyte motion [55]. Only the rotational part of the force can cause any change to the system by inducing convective flow which effectively reduces the diffusion layer thickness, and therefore increases mass transport to the electrode surface.

As the potential part has no effect on the electrolyte flow, only the *change* in electrolyte susceptibilities needs to be taken into account [23]. These susceptibility changes are mostly due to the change in concentrations of paramagnetic species, which in our case is $[Fe(CN)_6]^{3-}$ ions with one unpaired electrons ($\chi_{mol} \sim 6.5\times10^{-9}$ m^3 mol^{-1} [56]). The influence of diamagnetic species, $[Fe(CN)_6]^{4-}$ ions and H_2O molecules (no unpaired electrons, $\chi_{mol} = -1.6\times10^{-10}$ m^3 mol^{-1} [29]), can be neglected as magnetic susceptibilities of diamagnetic species are significantly smaller than paramagnetic species.

Note that this redox system was chosen as it only has *one* unpaired electron (upe) and hence has a small magnetic susceptibility so as to demonstrate that the magnetic gradient force effect is significant even for *weakly* paramagnetic species. For species with more unpaired electrons and hence higher paramagnetic susceptibilities such as high-spin

transition metal complexes Co^{2+} (3 upe), Ni^{2+} (2 upe) or Mn^{2+} (5 upe), greater mass transport enhancement is expected.

According to Mutschke et al. [23], the rotational part of the force calculated by taking the curl of the force ($\nabla\times\mathbf{f}_m$) given in eq. (4) can be simplified to

(10)

where Δc denotes the concentration change in the diffusion layer of thickness δ_c.

It is recognized that this rotational part of the magnetic gradient force will enhance mass transport within the diffusion layer (δ_c) because the concentration gradient (∇c) is significant only in the diffusion layer and tends towards zero in the bulk solution. At the same time, the magnetic field gradient ($\nabla\mathbf{B}$) is only significant in the close vicinity of the Fe_3O_4 NPs as shown in Fig. 9 for the variation of **B** with distance away from the NPs. The values of $\nabla\mathbf{B}$ drop from $>10^8$ T m^{-1} at $z<10$ nm to <1 T m^{-1} at $z>40$ nm (see SI for details). The magnetic field gradient force is therefore optimized in the diffusion layer and hence the flux to the electrode surface is increased by this phenomenon.

Figure 9 Simulation of a decay of magnetic flux densities generated from a fully magnetized 4 nm Fe_3O_4 NP with $\mathbf{B}(z = 4\text{ nm}) = 0.53$ T in an electrolyte solution of $\mu_r = 1$; see SM for simulation details

As described in the Theory section, eq. (5) can be used to assign which of the two magnetic forces is dominant. The Fe_3O_4 NPs have a specific magnetic length scale of ~7 orders of magnitude smaller than the external NdFeB magnet. The measured currents, however, did not show such a significant difference. This is because, as mentioned above, the magnetic gradient force only plays a significant role close to the surface of the Fe_3O_4 NPs. At this distance, the frictions between walls and the moving solution are very large that the effects of the force on mass transport are restricted, despite the force being extraordinarily large. The exact, quantitative predictions of the magnetic force-driven mass transport enhancement therefore have to be done via numerical simulation and are subjected to future work.

Additionally, opposed to one's intuition that the systems having paramagnetic species as starting materials such as the reduction of $[Fe(CN)_6]^{3-}$ would result in greater magnetic-driven mass transport enhancement than having them as reaction products, the observed current and charge enhancements are in the same order (~8%) for both the oxidation of $[Fe(CN)_6]^{4-}$ and the reduction of $[Fe(CN)_6]^{3-}$. This can be explained using equation (10). An important parameter that gives rise to the convective flow is the *change* in concentration of paramagnetic species, which upon 1-electron transfer processes, it is a given that either reactants or products would have unpaired electrons and hence would be paramagnetic. The magnetic field effects on mass transport are therefore similar for an oxidation or reduction of the same redox couples as demonstrated by the $[Fe(CN)_6]^{4-}/[Fe(CN)_6]^{3-}$ redox couple in this paper.

The Fe_3O_4 NPs are magnetized in the presence of external magnetic field and hence result in an enhanced mass transport as explained above. On the removal of an external NbFeB magnet, it is found that the chronoamperometric currents return to their initial values before the first placement of the magnet (see Fig. 8). This is consistent with Fe_3O_4 NPs being superparamagnetic which means that their magnetization shifted back to near zero upon the removal of an external magnetic field [57],

demonstrating that the enhanced mass transport can be turned 'on' or 'off'. This allows for controlled alteration of the mass transport to the electrode by a simple external switch.

To summarize the observed effect of magnetic fields on mass transport in the electrochemical systems under studies, the bar graphs in Fig. 10 combine the experimental results showing the evident enhanced mass transport in electrolyte solution when the electrodes are modified with Fe_3O_4 NPs in comparison with bare electrodes or electrodes modified with diamagnetic NPs, quantified by mass transport controlled currents and total charges measured via chronoamperometry. Figure 11 shows schematic representations of magnetic forces involved in the system when electrodes are modified with diamagnetic Au or Ag NPs (Fig. 11**a**) and magnetic Fe_3O_4 NPs (Fig. 11**b**).

Figure 10 bar graphs displaying **(a)** current and **(b)** charge enhancements in the chronoamperometric measurements

Figure 11 schematic representations of the magnetic forces involved

5 Conclusions

A new method has been developed to enhance mass transport in electrolyte solution using the magnetic gradient force as an alternative to high energy consumption flow cells, rotating disc electrodes or classical magnetohydrodynamics. Superparamagnetic iron oxide (magnetite, Fe_3O_4) nanoparticles are immobilized onto the electrode surface, allowing the generation of an ultra-high magnetic gradient (10^8 T m^{-1}) near the electrode. Magnetite nanoparticles are easy to make, non-toxic and chemically stable in many reaction conditions, benefiting practical uses in comparison to corrosive permanent magnets. Thanks to the superparamagnetic properties of these nanoparticles, mass transport can conveniently be controlled using an external magnetic field as a switch to turn the magnetic field gradient force on and off. This method is expected to be particularly interesting in spatially strongly confined systems, such as micro- and nanofluidic devices, where the implementation of conventional (mechanical) means of mass transport control is challenging.

Importantly, the magnetic gradient driven mass transport enhancement is not limited to paramagnetic reactants, but only requires that at least one of

the reaction partners has at least one unpaired electron – a condition that is fulfilled for almost any one-electron electrochemical reaction. The proof-of-concept redox couple used herein $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ comprises one and zero unpaired electrons, respectively, and an evident magnetic gradient field effect was observed even in the case of the thus comparably low paramagnetic susceptibilities. Reactants with larger number of unpaired spins, such as high-spin transition metal complexes Co^{2+}, Ni^{2+}, Mn^{2+}, comprise much larger paramagnetic susceptibilities and are therefore expected to show greater magnetic gradient force enhanced mass transport - an effect that will be explored in future work.

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Electronic Supplementary Material

Magnetic control – switchable ultra-high magnetic gradients at Fe_3O_4 nanoparticles to enhance solution-phase mass transport

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S 1: Characterization of nanoparticles

- **Fe_3O_4**

A representative TEM image of the Fe_3O_4 nanoparticles used and the analysis of their size distribution are given in Fig. 2e and 2f in the main text. A high-resolution TEM image of Fe_3O_4 nanoparticles is displayed in Fig. S1. The lattice parameters (d) observed were d = 0.257 nm, 0.245 nm and 0.210 nm, corresponding to the lattice parameters of Fe_3O_4 (from the Powder Diffraction File database) in the (3,1,1), (2,2,2) and (4,0,0) planes, respectively.

Figure S1 High-resolution TEM image of Fe_3O_4 nanoparticles; the lattice parameters observed were: **Nanoparticle 1**: d = 0.257 nm → d_{311} = 0.253 nm; **Nanoparticle 2**: d = 0.245 nm → d_{222} = 0.242 nm; **Nanoparticle 3**: d = 0.210 nm → d_{400} = 0.210 nm

- **Au**

The TEM analysis of the Au nanoparticles shown in Fig. 2a and 2b in the main text yields the size distribution of 12.9±3.5 nm radius. The size of the Au nanoparticles was confirmed using UV-Vis absorption spectroscopy. The absorption peak was observed at 519 nm (see Fig. S2), a wavelength of which has been reported by Ly et al. [1] using the same batch of Au nanoparticles to correspond to the size of 9.6±6 nm radius. Ly et al. also reported the DLS data revealing the size of Au nanoparticles to be 14.2 nm in radius, consistent with the TEM and UV-Vis measurements.

Figure S2 UV-Vis absorption spectrum of the Au nanoparticles

- **Ag**

The TEM analysis of the Ag nanoparticles shown in Fig. 2c and 2d in the main text yields the size distribution of 3.4±2.2 nm radius. These size distributions were in very good agreement with the UV-Vis and DLS data reported elsewhere [2].

S 2: Calculation of surface coverage

For a spherical NP, the charge ( ) can be calculated from

(S1)

where is the Faraday constant, is the number of electrons exchange per formula unit, is the density of the NP material, is the molar mass of the NP material and is the radius of the NP.

The number of NPs immobilized on the electrode surface is therefore described by

(S2)

where is the total stripping charge obtained from linear sweep voltammetry and is the stripping charge expected for one spherical NP.

The surface coverage ( ) in equation (6) in the main text can therefore be rearranged to

(S3)

The densities of Ag and Fe_3O_4 are 10.5 and 5.1 g cm^{-3} respectively [3].

S 3: Simulation of magnetic fields from NdFeB permanent magnet

In order to observe magnetic flux densities created from the permanent NdFeB magnet, simulations were performed with the numerical simulation software Amperes 9.0, using the 3D field solution, Finite Element solver in magnetostatic mode. The permanent magnet parameters employed were the remnant magnetic flux density of $\mathbf{B}_r$ = 1.35 T for sintered 45 MG Oe NdFeB magnet and the relative magnetic permeability of = 1 throughout the rest of the simulation space. The results obtained are shown in Fig. S3.

Figure S3 Magnitude of magnetic flux densities from the 45 MG Oe NdFeB magnet in the area of 15×15 mm^2 surrounds the position of the working electrode

From this simulation, it was found that the magnetic field gradient ( ) of the NdFeB permanent magnet was in the order of 1×10^{1} T m^{-1} in the region containing the working electrode (15 mm away from the NdFeB magnet and the electrode is 3 mm in diameter).

S 4: Simulation of magnetic fields from Fe3O4 nanoparticles

Simulations were performed with an Intel® Xeon® E5-1620 processors (3.70 GHz) using the software package COMSOL Multiphysics® version 5.0 [4]. The spatial grid densities were set as "Physics-Controlled Meshing." The Magnetic Fields, No Currents, 2D axisymmetric model was used to solve the variation of magnetic flux density as a function of distance away from the surface of the magnetic Fe_3O_4 NP of size 4 nm in radius according to eqn. S4 and S5.

(S4)

(S5)

The magnetic flux density at the surface of the Fe_3O_4 NP was set to 0.53 T and the relative magnetic permeability was set to one throughout the entire simulation space (= 1).

a) **b)**

Figure S4 a) 2D axisymmetric simulation space **b)** magnetic flux densities from the 4 nm radius Fe_3O_4 NP

The simulation shows ultra-high magnetic field gradient ( ) in the close vicinity of the Fe_3O_4 NPs as the values of are $>10^{8}$ T m^{-1} at $z<10$ nm. The gradient drops quickly with distance from the NP surface to <1

T m^{-1} at z>40 nm, as stated in the main text. Figure 9 was also a result arising from this simulation.

S 5: Derivation of magnetic gradient forces

The magnetic gradient force ( ) is described by [5]

(S6)

where is the vacuum permeability (= 4 $\times 10^{-7}$ V s (A m)$^{-1}$). and are the magnetization and magnetic field strength of magnetic Fe_3O_4 NPs in the presence of an external NdFeB magnet respectively.

According to the following relations between , and :

(S7)

and

(S8)

where is the magnetic flux density (or magnetic induction) and is the total susceptibility of the solution ( ), equation (S6) can be simplified to [6]

(S9)

For the electrochemical set-up presented in this paper (a closed cell), the potential (irrotational) part of the force would press against the wall and hence have no effect on electrolyte motion [7]. Only the rotational part of the force can cause any change to the system by inducing a convective flow which effectively reduces the diffusion layer thickness, and therefore increases mass transport to the electrode surface.

As the potential part has no effect on the electrolyte flow, only the *change* in electrolyte susceptibilities needs to be taken into account [6]. These susceptibility changes are mostly due to the change in concentrations of paramagnetic species, $[Fe(CN)_6]^{3-}$ in our case (~ 6.5×10^{-9} m^3 mol^{-1} [8]), and the diamagnetic influence of diamagnetic $[Fe(CN)_6]^{4-}$ ions and H_2O molecules (= -1.6×10^{-10} m^3 mol^{-1} [9]) can be neglected.

According to Mutschke et al. [6], the rotational part of the force calculated by taking the curl of the force

( ) results in the following expression:

(S10)

where and are the molar susceptibility and concentration of the $[Fe(CN)_6]^{3-}$ ions respectively.

Equation S10 can be simplified to [6]

(S11)

where denotes the concentration change in the diffusion layer of thickness .

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