

Quantitative electrophoretic deposition of nanocrystal films from
non-aqueous suspensions

by

Krishna Raj Panta

B.Sc. Trivbhuvan University, Kathmandu, Nepal, 2008

M.Sc. Tribhuvan University, Kathmandu, Nepal, 2010

AN ABSTRACT OF A DISSERTATION

submitted in partial fulfillment of the
requirements for the degree

DOCTOR OF PHILOSOPHY

Department of Physics
College of Arts and Sciences

KANSAS STATE UNIVERSITY
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Abstract

This study presents a novel method to correlate the mass and charge transfer kinetics during the electrophoretic deposition of nanocrystal films by using a purpose-built double quartz crystal microbalance combined with simultaneous current-measurement. Our data support a multistep process for film formation: generation of charged nanocrystal flux, neutralization via charge transfer at the electrode, and polarization of neutral nanocrystals near the electrode surface. The neutralized particles are then subject to dielectrophoretic forces that reduce diffusion away from the interface, generating a sufficiently high neutral particle concentration at the interface to form a film. The correlation of mass and charge transfer enables quantification of the nanocrystal charge, the fraction of charged nanocrystals, and the initial sticking coefficient of the particles. These quantities permit calculation of the film thickness, providing a theoretical basis for using concentration and voltage as process parameters to grow films of targeted thicknesses.

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Approved by:

Major Professor
Bret Flanders

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Dedication

To my daughter Evana, son Aayu, wife Anju, and parents.

Chapter 1

General Introduction

The growing need for miniaturized structures [1] demands uniform, thin, and robust films of organic, inorganic, and biomaterials on substrates. The goal is to fabricate controlled-structures applicable for drug delivery [2], tissue engineering [3], and high demand gas sensors [4]. A second, but prominent field is the synthesis of nanoparticle thin-film-structures. Size tunable properties [5; 6] and low integration cost into devices make them promising candidates for nanoelectronics [7], light-emitting devices [8], fiber-optic sensors [9], ultrahigh-density data storage media [10], and optoelectronics [11; 12]. Nanoparticle superlattice structures assembled by utilizing shape, size, and ligand tunable functionality find their applications in electronics, photovoltaics, and sensing applications [13–16]. There are also nanocrystalline diamond thin films that are promising candidates for various applications: electrochemistry, heat spreaders, sensor devices, and protective coating [17]. These structures, based on a bottom-up approach, involve stamping controlled-nanoparticle-structures on substrates. Despite much work for the controlled synthesis of the nanoparticle films, the emergence of general techniques for their assembly is still lacking—a major hurdle for nanoparticle films to find their applications in day-to-day technological films.

In industrial settings, vapor phase techniques dominate the synthesis of thin films. Those techniques include: chemical vapor deposition (CVD) [18], e-beam physical vapor deposition [19], magnetron sputtering [20] and ion-beam sputtering (IBS) [21]. These methods share

a common technique of decomposing target material into an atomic flux that is directed onto a substrate during the deposition process. For example, in the conventional sputtering process, a jet of energetic noble gas ions (Argon) bombards (Figure 1.1) a target material to expel ionized atoms from its surface. An external field directs these sputtered target ions on the substrate to form a thin film. This method involves transforming target material into the gaseous form prior to deposition which makes it unfit for the complex, organic, and biological materials [22]. To deposit complex materials, simple solution-based methods are better alternatives as most of the nanoparticles, organic molecules, vesicles, and living cells are best handled in the liquid phase. The existing widely used methods based on solution-phase include dip-coating [23], spin-coating [24], layer-by-layer assembly [25] and solvent evaporation [26]. These methods lack direct control over the particle flux during film growth, which impairs control over the growth rate, thickness, and morphology of the deposits. There are also Langmuir Blodgett methods [27] that are highly precise, producing mono-molecular films of arbitrary densities, but which are largely restricted to amphiphilic films of single monolayer thickness.

Electric field-assisted assembly known as electrophoretic deposition (EPD) is a promising method that addresses the above-mentioned problems. In 1808, Russian scientist Ruess first observed that clay particles in water are influenced by the applied electric field. In 1940, Hammaker used this idea to deposit ceramic materials in the solution phase on the surface of electrodes using an electric field. Since then, EPD is gaining popularity and nowadays this solution-based tool is in use for a wide range of applications in both academic and industrial settings. Recent works have demonstrated its versatility by depositing uniform coatings on arbitrary shaped electrodes [28], coating of composite materials [29], and carbon nanotube thin films [30]. One of the reasons EPD is so popular among the scientific community is because it is cost-effective and requires a simple apparatus. Moreover, EPD is useful to deposit metal, oxides, and semiconductors in electrode surfaces of any shape with minimal changes in the design and positioning of electrodes. This method uses an electric field to precisely control the flux of depositing particles, provided they are charged, which demonstrates its application in the controlled growth and quantification of nanoparticle film assembly.

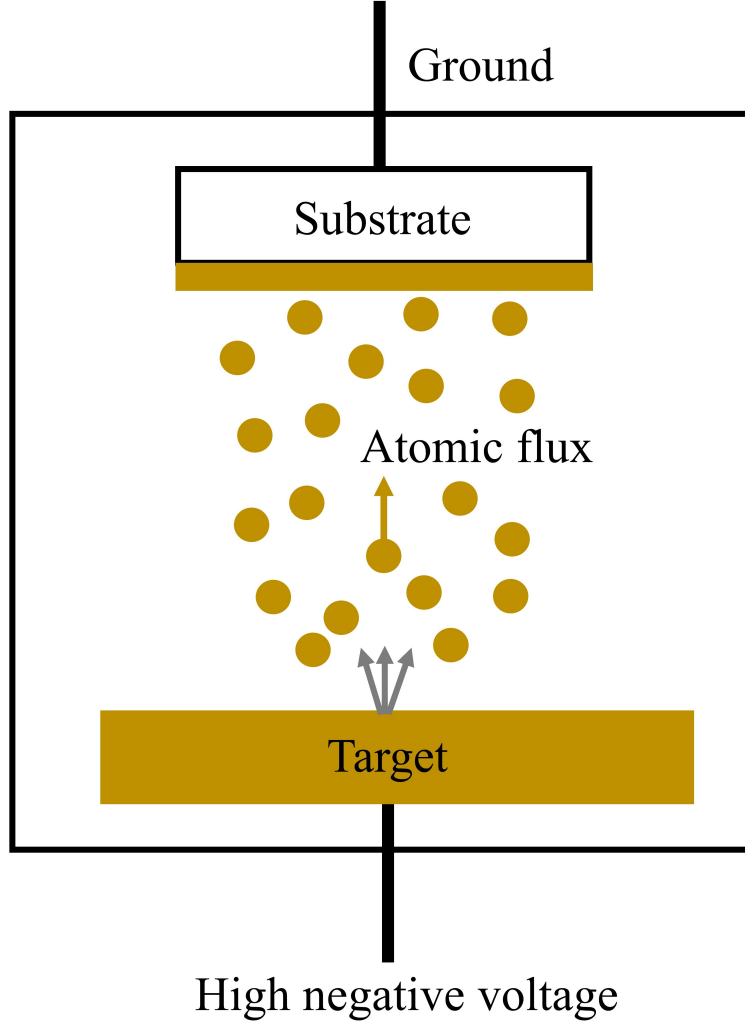


Figure 1.1: *Schematic of sputtering process.*

In principle, the externally applied electric field drives the positively and negatively charged nanocrystal in the suspension to their respective electrodes and deposits on the surface of electrodes. Over the past years, E-field assisted assembly has found applications in preparing high-quality films of various thicknesses in a controlled manner [31; 32], and micropatterns [33]. To prepare such quality films, good control over the nanocrystal flux is required. In this venue, electric field-assisted assembly of nanocrystal film emerges as it provides better control over the nanocrystal flux depositing on the substrates. This flux control is imperative to understand the overall deposition mechanism and hence to quantify the major parameters of film assembly.

In this thesis, we present the E-field assisted assembly of nickel nanocrystal suspended in an organic solvent. Here we monitor the growth of mass *in situ* on both anode and cathode simultaneously with the current. This measurement finds a novel way to correlate the mass and charge transfer kinetics. This correlation will allow us to quantify the important film growth parameters: nanocrystal charge, the fraction of charged nanocrystals, and the initial sticking coefficient. These determinations will finally lead us to predict the final film thickness using the process parameters: concentration and voltage.

1.1 Parameters of EPD

The mechanism of EPD is the drift of charged particles suspended in the solvent under the application of an external electric field. Thus, the EPD process can be controlled either by suspension-related parameters or by process-related parameters. The suspension-related parameters include particle size, the viscosity of the suspension, the dielectric constant of solvent used, and the charge on the dispersed particles. The process parameters involve deposition time, applied field, bulk concentration, etc. The mathematical expression to correlate the number of particles deposited per unit time (normalized by electrode area, A), $\frac{\dot{N}}{A}$, during electrophoretic deposition is the product of the sticking coefficient, (s), and the particle flux. Since the particle flux is given by the product of charged particle density, (fc_b) (where f is the fraction of particles that are charged and c_b is the bulk concentration), and its drift velocity, (v), the normalized growth rate takes the form,

$$\frac{\dot{N}}{A} = (\text{sticking coefficient})(\text{charge density})(\text{drift velocity}). \quad (1.1)$$

The drift velocity is the product of particle mobility, (μ), and the applied electric field, (E). The mobility, μ , is given by $\mu = ze/3\pi\eta d_H$. Where η is the viscosity of solvent and d_H is the particle diameter. So, equation 1.1 becomes,

$$\frac{\dot{N}}{A} = \frac{e}{3\pi\eta d_H} (fsz)c_b E. \quad (1.2)$$

The equation 1.2 is known as the Hamaker equation for EPD. It is the expression for growth rate in terms of particle level properties (f , s , z , and d_H), the solvent property (ν), and process parameters (c_b and E).

1.1.1 Suspension parameters

The water-based suspensions are environmentally friendly and need a much lower field than organic-based suspensions, however, they are not generally suitable for electrophoretic deposition. The major problem with aqueous suspension is the possible electrochemistry at the electrode surface. This will impair the efficiency of the entire process and the quality of the deposit. The common electrochemical reactions happening at anode and cathode in case of water-based suspensions are $2H_2O \rightarrow O_2 + 4H^+ + 4e^-$ and $2H_2O \rightarrow H_2 + 4OH^- + 2e^-$. So, during electrodeposition, the evolution of oxygen and hydrogen are likely causes of impairing film quality [34; 35]. Therefore, organic solvents are considered superior to water as dispersing media for electrophoretic deposition.

The electrophoretic mobility in solvents with similar dielectric constants varies significantly depending on the viscosity of the solvent. In the study of the deposition of ceramic particles in the porous substrate, it has been found that the improvement in the penetration of material using the solvent of high dielectric constant and low viscosity. It has shown that the addition of dopant changes the viscosity of solvent [36]. The optimum amount of dopant is needed to keep the viscosity of the solvent low which helps the particles in suspension arrange themselves in optimized locations in suspension under electrostatic attraction. Another study used hydroxyapatite nanoparticles [37] to investigate deposition rates in a series of alcoholic suspensions. This study found that the deposition rate is higher in the suspension of lower molecular weight.

In general, the good solvent is the one that dissolves/suspends the particles. In addition to that, desirable solvent properties are low viscosity, high dielectric constant, and low conductivity [38]. The physical properties of organic solvents which are commonly used in electrophoretic deposition are given in the table 1.1.

Table 1.1: *Physical properties of general solvents*

Solvents	Viscosity (cP)	Dielectric constant	Citation
n-Propanol	1.936	20.33	[39]
Acetone	0.308	20.7	[40; 41]
Ethanol	1.09	24.55	[42; 43]
Methanol	0.56	32.63	[43; 44]
n-butanol	2.587	17.51	[43]
Iso-propanol	2.04	19.92	[45]
Ethylene glycol	16.265	37.7	[46]
Toluene	0.56	2.38	[47]
Hexane	0.27	1.88	[48]

1.1.2 Deposition time and field

At fixed voltage EPD, the thickness of the deposited film increases with time. Generally, the film grows initially at a maximum rate on the electrode surface, and its thickness scales linearly with time [49]. At a later time, the growth rate decreases gradually with time [50; 51] and finally stops growing after attaining a certain film thickness [49]. This is expected because the voltage drop across the bulk of the cell decreases as the film thickens. The formation of an insulating layer on the electrode surface is one of the causes of the low voltage drop in the bulk and hence the lower growth rate at a later time [52].

Another reason for the weakening of growth rate with time, which this thesis discusses, is screening. At time zero when the field is just turned on, the distribution of charged nanocrystals is uniform throughout the suspension making the nanocrystal density homogeneous. Thus, at an early time, the electric field is uniform between the electrodes. During the film growth at the electrode, nanocrystals in the suspension redistribute in response to the applied electric field so that the density of charged nanocrystals becomes inhomogeneous between the electrodes. Therefore, at a later time, the cell differentiates into an interfacial region and a bulk-like region. The interfacial region is composed of nanocrystal film and mobile-charged carriers. The nanocrystal film might have some charged nanocrystal embedded in it and the screening due to those charges is analogous to Thomas-Fermi screening while the mobile charge carriers near the electrode surface give rise to Debye screening. In both cases, we expect the electric field to decay exponentially with the distance from the electrode surface while at the bulk the electric field is nearly constant.

The electric field is another important parameter in electrophoretic deposition and plays a critical role in setting the final thickness and quality of deposited films. The film thickness in general increases with the strength of the applied field. The hydroxyapatite film deposited on the $\text{Ti}_6\text{Al}_4\text{V}$ substrate follows this rule [52]. There are situations where uniform films were deposited at a moderate field (25-100 V/cm), whereas the quality of film worsens if a relatively stronger field ($> 100\text{V/cm}$) is applied [51]. The poor-quality film at the higher field is due to the turbulence in the medium thereby disrupting the film deposition and also

the high particle velocity of impinging particles on the electrode surface makes them difficult to find the optimized location on the electrode surface.

1.2 Review of Literature on Nanocrystal Films Grown by EPD

It has been found that nanocrystals composed of materials such as metal, semi-conductor, and ferrimagnetic are more common for nanocrystal research. The nanocrystal size in the systems we reviewed ranges from 2.3 nm to 175 nm. These studies used different ligand types (Oleic acid, n-trioctylphosphine, trioctylphosphine, polyethyleneimine) to stabilize the nanocrystal in the suspension. The solvents they used as a dispersion media are Hexane, Toluene, Isopropanol, Octane, Chloroform, Methanol, and their mixtures. The electric field was applied to direct depositing nanocrystal onto targeted substrates. Most of the studies applied an electric field of magnitude $\sim 10^5$ V/m resulting in films of thickness ranging from 3 nm to 2000 nm. Metallic nanocrystals such as silver nanocrystals (~ 7 nm in diameter) dispersed in Toulene produced 3D superlattice structures. It has been shown that magnetic nanocrystal (iron oxide) gives a wide range of film thickness ranging from monolayer to ~ 500 nm. The summary of the literature review including nanocrystal size, composition, and ligand type; solvent used; EPD parameters; and film thickness is presented in the table [1.2](#).

Table 1.2: Summary of literature review

Nanocrystal size, composition/ligand(additive)	solvent	EPD parameters: Applied field, concentration, and time	Film thickness	Citation
14 – 20 nm, Ni/OA	Hexane	200 – 2360 V/m, 4.22×10^{20} - 4.19×10^{21} nanocrystals/m ³ , ~ 50 s	Sub-monolayer-60 nm	This work
3.4 nm, CdSe/TOPO; 12 nm, γ -Fe ₂ O ₃ /OA; 2.3 nm, Au/dodecanethiol	Hexane	2.65 $\times 10^5$ V/m, CdSe (3.1×10^{14} dots/cc); Fe ₂ O ₃ (5.2×10^{12} dots/cc); Au (2.4×10^{13} dots/cc); 20 min	500 nm	[53]
3.3 nm, TiO ₂	Hexane	3.33×10^5 V/m, 8.6×10^{22} NC/cm ³ , 40–240 s	3.1 – 15.4 nm	[54]
2.5 – 4.5 nm, ZnO	1:5 Ethanol and Chloroform	1000 – 3333 V/m, 8 – 24 μ M, 1 – 60 min	1 – 200 nm	[55]
50 nm, B ₄ C/PEI	Isopropyl alcohol	10000 V/m, 1 g/L, 20 min	————	[56]
155 – 175 nm, TiO ₂	Pentanol, Hexanol	5000 V/m, 6 g/L, 20–80 s	————	[57]

Continued on next page

Table 1.2 – *Continued from previous page*

Nanocrystal size, composition/ligand(additive)	solvent	EPD parameters: Applied field, concentration, and time	Film thickness	Citation
2.4 nm, Eu ₂ O ₂ /OA	Hexane	50000 V/m, $2 \times 10^{15} NC/cm^3$, 15 min	110 nm	[58]
3.6 nm, CdSe/TOPO	Hexane	2.65×10^5 V/m, 3×10^{14} dots/cc, 30 min	550 nm	[59]
4.8 nm, ZnO (NaOH)	Isopropyl alcohol	1000 – 5000 V/m, 11500 s	5 – 135 μm	[60]
17 nm, FeO/Fe ₃ O ₄ core-shell	Hexane	10000 V/m, 1 mg/ml, 20 – 140 s	Monolayer films	[61]
3.2 nm, CdSe/carboxylate (tetramethylammonium hydroxide)	Water, Methanol (80/20 by volume)	40 – 80 V/m, $\sim 10^{13}$ particles/ml, 1 – 10 min	Deposition into nanopores	[62]
14.8 nm, Fe ₃ O ₄ /OA, oleylamine	Hexane, Toluene, Chloroform	1.0×10^5 V/m, 0.5 mg/ml, 15 min	200 – 1400 nm	[63]
7.1 nm, Ag/dodecanethiol	Toluene	14 – 87 V/cm, 6 mg/ml, 5 – 55 min	Formation of superlattice	[64]
6.6 nm, Ag/dodecanethiol	Toluene	400 V/cm, 4 mg/ml, 30 min	Formation of superlattice	[65]
10.7 nm, Co/OA	Hexane	500 V, 1 mg/ml, 50 s	77 nm	[66]

Continued on next page

Table 1.2 – *Continued from previous page*

Nanocrystal size, composition/ligand(additive)	solvent	EPD parameters: Applied field, concentration, and time	Film thickness	Citation
2.3 – 5.0 nm, CdSe/(TOPO, TOP)	Hexane, Octane (9:1 by volume)	500 V, $\sim 10^{15}$ nanocrystals/ cm^3 , ~ 30 min	1000 – 2000 nm	[67]
10.8 nm, 12.3 nm, iron oxide/OA, cobalt ferrite/OA	Hexane	10000 V/m, 10^{17} NP/ml, 60 s	Monolayer films	[68]
9.6 nm, iron oxide/OA	Hexane	1.0×10^5 V/m, 0.1 mg/ml, 15 s	Monolayer films	[69]
6.85 nm, PbSe/OA	Toluene, acetonitrile (5:1 by volume)	20000 V/m, 4 – 5 mg/ml, 10 s	500 nm	[70]

Chapter 2

Theory

We are interested in solution-based deposition of nanocrystal films achieved by directing a flux of nanocrystals onto a targeted substrate. The form of this method matches that of several widely used gas-phase methods for thin film deposition, such as sputtering. Attaining quantitative control over film growth with our EPD-based approach requires characterization of the relationship between the flux of particles in the solution and the growth rate of the film. Here we present theory that relates these quantities.

2.1 Theory for Electrophoretic Deposition

In electrophoretic deposition, the applied field drives the charged particles to their respective electrodes. We illustrate this process for the anodic electrode in Figure 2.1a. The moving charged particles give rise to a measurable current density while the nanocrystal film is growing. If the nanocrystals are the only charge carriers in the system, we can gain insight into film-formation by monitoring the current density, as others have illustrated elsewhere [71]. The applied field also drives the deposition of particles onto the substrate to form a film, as illustrated in Figure 2.1b for the anode. Therefore, one can also monitor the growth rate of the film in real-time by monitoring the growth of mass on a given electrode. This quantity is a film-specific property, unlike current density which is a whole-system property.

Next, we relate the growth rate of the film to the flux of incoming particles.

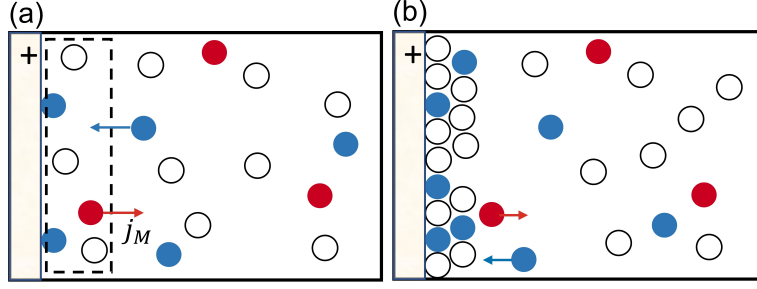


Figure 2.1: (a) Schematic showing the drift of positive (red) and negative (blue) nanocrystals in response to the applied field. The dashed rectangle is the Gaussian pillbox used to evaluate (2.4). (b) Schematic showing film-formation.

Ampere's Law relates the current density j to a changing electric field E and a magnetic field B :

$$\nabla \times B = \mu_0 j + \epsilon_0 \mu_0 \frac{\partial E}{\partial t}, \quad (2.1)$$

where μ_0 and ϵ_0 are the permeability and the permittivity of free space respectively. Taking the divergence of both sides of (2.1), and recalling that $\nabla \cdot (\nabla \times B) = 0$, gives:

$$\nabla \cdot j = -\dot{\rho}, \quad (2.2)$$

where we have invoked Gauss's Law: $\nabla \cdot E = \frac{\rho}{\epsilon_0}$. ρ is the total charge density, and the overdot denotes time differentiation.

With respect to the Gaussian pillbox in Figure 2.1a, Equation (2.2) says that the charge in the pillbox will change due to the flow of currents into and out of the pillbox. For the case where the nanoparticles are the only charge carriers, the charge density, ρ , is generally expressed as

$$\rho = \sum_p z_p e \frac{N_p}{V} - \sum_q z_q e \frac{N_q}{V}, \quad (2.3)$$

where p and q are indices that label the positive and negative nanoparticle species, respectively. z_p and z_q are the charges on species p and q , respectively. N_p is the number of positive species p , and N_q is the number of negative species q . V is volume of the box. The negative

sign in the second term, $-\sum_q z_q e \frac{N_q}{V}$, reflects the negative character of the charges labeled q . For the special case of the particles having a single charge state such that the summations over p and q are unnecessary, this expression simplifies to $\rho = z_p e \frac{N_p}{V} - z_q e \frac{N_q}{V}$. Substituting this expression into (2.2) yields

$$\nabla \cdot j = -\frac{z_p e \dot{N}_p}{V} + \frac{z_q e \dot{N}_q}{V}. \quad (2.4)$$

We consider here two periods of film-growth: the initial time immediately following the voltage-step application (this Section) and the steady-state limit at long times when the film no longer grows but current still flows (Section 2.3).

Figure 2.1a depicts the initial situation. Current flow due to charged particle migration has just started, so there is negligible screening at the electrodes. Thus, the field is uniform across the cell ($\frac{V}{L}$), and the particle densities are homogeneous. For these reasons, we neglect charge transfer at the electrode interfaces, as well as other field-dependent processes, and consider only charged particle migration towards the electrodes, as depicted by the arrows in Figure 2.1a. Volume integration of Equation 2.4 with respect to the Gaussian pillbox in Figure 2.1a gives:

$$j_M = -\frac{z_p e \dot{N}_p}{A} + \frac{z_q e \dot{N}_q}{A}, \quad (2.5)$$

where j_M denotes *migration* current density and A is the cross-sectional area of the box. The migration current density is generally expressed as

$$j_M = \sum_p z_p e n_p \mu_p E + \sum_q z_q e n_q \mu_q E. \quad (2.6)$$

A positive value for j_M corresponds to the rightward flow of positive particles and the leftward flow of negative particles, as depicted in Figure 2.1a. For the current case where the particles have single charge states p and q , j_M simplifies to $j_M = z_p e n_p \mu_p E + z_q e n_q \mu_q E$. Substituting

this expression into Equation 2.5 yields

$$\frac{-z_p e \dot{N}_p + z_q e \dot{N}_q}{A} = z_p e n_p \mu_p E + z_q e n_q \mu_q E. \quad (2.7)$$

Equation 2.7 shows that the applied field E drives a flux of particles of charge z_q into the pillbox ($\frac{+\dot{N}_q}{A}$) and a flux of particles of charge z_p out of the pillbox ($\frac{-\dot{N}_p}{A}$).

To a predominant extent, only the negative particles will deposit on the anode. Thus, the flux $\frac{\dot{N}_q}{A}$ into the pillbox is equivalent to the flux onto the anodic film. The ratio of the flux of particles that successfully deposit on the anodic film ($\frac{\dot{N}_{an}}{A}$) to the total flux of particles impinging on the film ($\frac{\dot{N}_q}{A}$) is termed as the anodic *sticking coefficient* s_q . We express s_q as:

$$s_q = \frac{\dot{N}_{an}}{\dot{N}_q}. \quad (2.8)$$

$\dot{N}_{an}$ is the growth rate of the anodic film, the quantity we seek. Matching the terms in Equation 2.7 that are labeled by q results in $\frac{\dot{N}_q}{A} = n_q \mu_q E$. Invoking Equation 2.8 yields:

$$\frac{\dot{N}_{an}}{A} = s_q n_q \mu_q E. \quad (\text{anode}) \quad (2.9a)$$

The analogous analysis at the cathode yields:

$$\frac{\dot{N}_{ca}}{A} = s_p n_p \mu_p E. \quad (\text{cathode}) \quad (2.9b)$$

These are the desired results: equations that relate growth rate and flux. That is, relationship 2.9a equates the growth rate $\dot{N}_{an}$ of the anodic film to the fraction s_q of the anionic flux $n_q \mu_q E$ that impinges upon the interface. Likewise, relationship 2.9b equates the growth rate $\dot{N}_{ca}$ of the cathodic film to the fraction s_p of the cationic flux $n_p \mu_p E$ that impinges upon the interface.

2.2 Method of Data Analysis

The theoretical linear relationships between growth rate and applied field (Equations 2.9a and 2.9b) indicate that the field can be used to control film growth. However, in order to advance our capability to the point where we can accurately predict the properties of a film, such as growth-rate and film-thickness, based on the process-parameters of the system (such as particle concentration, applied voltage, and time), methodology for using Equations 2.9a and 2.9b to analyze mass and current density data is needed. Generally, quantitative EPD requires knowledge of the number of charged species, the charge of each species, their individual concentrations, and their individual sticking coefficients. Next, we demonstrate the method by which we extract these quantities from our early time measurements.

2.2.1 Single charged species at time-zero

Here we illustrate our method for determining these quantities for the case of a single positive species and a single negative species during the early-time period of film-formation. To procede, we rewrite Equation 2.9a as,

$$\frac{\dot{N}_0^{anode}}{A} = s_q(0)(f_q c_b) \mu_q E_0, \quad (2.10)$$

where f_q denotes the fraction of negative species that are charged, $s_q(0)$ is the sticking coefficient of species q at time-zero, and c_b is the bulk nanocrystal concentration. The growth rate at the cathode has a similar form except with positively charged species. The mobility of the species q , μ_q , can be written as $|z_q|e/3\pi\nu d_H$ where z_q is the charge on the species q , e is the electron charge, ν is the viscosity of solvent, and d_H is the hydrodynamic diameter of the particle. Substituting for μ_q in Equation 2.10 yields

$$\frac{\dot{N}_0^{anode}}{A} = \frac{e}{3\pi\nu d_H} (s_q(0) f_q |z_q|) c_b E_0. \quad (2.11a)$$

The analogous expression for the cathodic growth-rate is

$$\frac{\dot{N}_0^{cathode}}{A} = \frac{e}{3\pi\nu d_H} (s_p(0)f_p z_p) c_b E_0. \quad (2.11b)$$

Equation 2.11a suggests that our measured mass-data (which provide the growth rates) will collapse to a line when the normalized growth rate, $\frac{\dot{N}_0^{anode}}{A}$, is plotted against $e/(3\pi\nu d_H)c_b E_0$. The plot will have a slope of $(s_q(0)f_q|z_q|)$.

Similarly, the current density at early times, j_0 , for single types of positive and negative species, using Equation 2.6 can be written as,

$$j_0 = e(f_q\mu_q|z_q| + f_p\mu_p z_p) c_b E_0, \quad (2.12)$$

where f_q and f_p denote the fractions of negatively and positively charged species respectively, and c_b is the bulk nanocrystal concentration. The mobilities for negative species q having charge z_q and positive species p having charge z_p are given by $\mu_q = \frac{|z_q|e}{3\pi\nu d_H}$ and $\mu_p = \frac{z_p e}{3\pi\nu d_H}$ respectively. Substituting the expressions for μ_q and μ_p in Equation 2.12 yields:

$$j_0 = \frac{e^2}{3\pi\nu d_H} (f_q z_q^2 + f_p z_p^2) c_b E_0, \quad (2.13)$$

Equation 2.13 suggests that the current density when plotted against $\frac{e^2}{3\pi\nu d_H} c_b E_0$ will collapse to a line with a the slope of $(f_q z_q^2 + f_p z_p^2)$.

If the particles are the only charge carriers, we can compare the growth-rates with current density by expressing the current density in terms of the sum of growth rates at anode and cathode. By multiplying Equation 2.13 by $\frac{s_q(0)f_q|z_q| + s_p(0)f_p z_p}{s_q(0)f_q|z_q| + s_p(0)f_p z_p}$, a factor of unity, and using expressions 2.11a and 2.11b, we can re-write Equation 2.13 as:

$$j_0 = m \frac{e}{A} [|\dot{N}_0^{anode}| + |\dot{N}_0^{cathode}|], \quad (2.14)$$

where the slope m is given by,

$$m = \frac{f_q z_q^2 + f_p z_p^2}{s_q(0) f_q |z_q| + s_p(0) f_p z_p}. \quad (2.15)$$

The quantity m can be determined from a plot of the independently measurable quantities, j_0 versus $\frac{e}{A} [|\dot{N}_0^{anode}| + |\dot{N}_0^{cathode}|]$. The quantity m depends on six independent variables. However, the values are constrained with sticking coefficients, $0 \leq s_p(0) \leq 1$, $0 \leq s_q(0) \leq 1$, and fraction charged, $f_p + f_q \leq 1$, whereas $z_p \geq 1$ and $|z_q| \geq 1$. If the slope, m , is unity, then $s_p(0)$, $s_q(0)$, z_p and $|z_q|$ must all equal unity. This conclusion follows from the quadratic charge dependence in the numerator and the linear charge dependence in the denominator, causing the numerator to increase faster with z than the denominator unless $z = 1$. With s and z set to one, the initial fraction of negative particles in the suspensions can be determined from the slope of Equation 2.11a. The initial fraction of positive particles in the suspension can be determined analogously.

2.2.2 Multiple charged species at time-zero

In this section we generalize the discussion in the previous section for the case of multiple positive species and multiple negative species. For negatively charged nanocrystals depositing on the anode, the anodic growth rate is:

$$\frac{\dot{N}_0^{anode}}{A} = \sum_q s_q(0) (f_q c_b) \mu_q E_0, \quad (2.16a)$$

where the sum is over the negatively charged species q , f_q is the fraction of negatively charged species q , $s_q(0)$ is the sticking coefficient of negative species q at time-zero, and c_b is the bulk

concentration. Similarly, the cathodic growth rate is:

$$\frac{\dot{N}_0^{cathode}}{A} = \sum_p s_p(0)(f_p c_b) \mu_p E_0, \quad (2.16b)$$

where the sum is over the positively charged species p , f_p is the fraction of positively charged species p , and $s_p(0)$ is the sticking coefficient of positive species p at time-zero. Substituting for the mobility of negative species q , in Equation 2.16a and expanding the sum by substituting the explicit negative charge-values $|z_q| = 1, 2, 3, \dots$ yields:

$$\frac{\dot{N}_0^{anode}}{A} = (s_{-1}(0)f_{-1} + 2s_{-2}(0)f_{-2} + 3s_{-3}(0)f_{-3} + \dots) \frac{e}{3\pi\nu d_H} c_b E_0, \quad (2.17a)$$

where the negative sign in the subscripts classify the quantity as a property of a negative particle. Likewise, substituting for μ_p and the explicit charge values $z_p = 1, 2, 3, \dots$ in Equation 2.16b yields

$$\frac{\dot{N}_0^{cathode}}{A} = (s_1(0)f_1 + 2s_2(0)f_2 + 3s_3(0)f_3 + \dots) \frac{e}{3\pi\nu d_H} c_b E_0. \quad (2.17b)$$

For multiple positive and negative species, the current density is written as,

$$j_0 = \left(\sum_q f_q c_b \mu_q |z_q| e + \sum_p f_p c_b \mu_p z_p e \right) E_0 \quad (2.18)$$

Substituting the mobilities for negative species q and positive species p in Equation 2.18 and expanding the sum by substituting in the explicit negative charge-values $|z_q| = 1, 2, 3, \dots$ and positive charge-values $z_p = 1, 2, 3, \dots$ yields:

$$j_0 = [(f_{-1} + f_1) + 4(f_{-2} + f_2) + 9(f_{-3} + f_3) + \dots] \frac{e^2}{3\pi\nu d_H} c_b E_0. \quad (2.19)$$

Combining equations 2.17a, 2.17b, and 2.19 (as we combined (2.11a), (2.11b), and (2.13) in sub-section 2.2.1), we can write,

$$j_0 = m \frac{e}{A} \cdot [|\dot{N}_0^{anode}| + |\dot{N}_0^{cathode}|], \quad (2.20)$$

where m is given by,

$$m = \frac{(f_{-1} + f_1) + 4(f_{-2} + f_2) + 9(f_{-3} + f_3) + \dots}{(s_1(0)f_1 + s_{-1}(0)f_{-1}) + 2(s_2(0)f_2 + s_{-2}(0)f_{-2}) + 3(s_3(0)f_3 + s_{-3}(0)f_{-3}) + \dots}. \quad (2.21)$$

Equation 2.21 has many undetermined variables. The terms in the numerator have the form of $z^2 f$ while those in the denominator have the form of $z s f$. As $z \geq 1$ and $s \leq 1$, the numerator will be larger than the denominator unless all high order terms are negligible. Thus, observing that $m \cong 1$ would indicate negligible high order terms and that $s_+ = s_- = 1$. This finding would give $m = \frac{f_+ + f_-}{f_+ + f_-} = 1$. Furthermore, a (near) unity slope of Equation 2.21 would also indicate that (predominantly) only single charged species are present in the suspension.

2.3 Thickness of the Terminal Film

At long times, film-growth stops although a steady flow of current continues. To analyze this steady-state, we will consider charge and particle number conservation in the interfacial regions of the electrodes and integrate the resulting continuity equation to attain an expression for the steady-state film thickness.

Figure 2.2a depicts this steady-state period. Considering conservation of particle number with respect to the pillbox of Figure 2.2a, we obtain a continuity equation for the total density of particles in the pillbox n_{tot} :

$$\nabla \cdot J_{tot} = -\dot{n}_{tot}, \quad (2.22a)$$

where J_{tot} is the total particle flux into the pillbox. For a static film, $\dot{n}_{tot} = 0$, so Equation

2.22a gives:

$$J_{tot} = 0. \quad (2.22b)$$

As we next discuss, we consider migratory, dielectrophoretic, and diffusive contributions to J_{tot} for the charged and neutral particle types. The dashed rectangle denotes a Gaussian pillbox, the outer surface of which is adjacent to the film surface. Particles may only cross the right side of the box.

Next, we will use Figure 2.2a to discern the relevant processes for this analysis. The steady, finite current-flow implies that leftward migration of negative charge and rightward migration of positive charge must occur, so our analysis will consider migration fluxes of positive and negative particles, $J_{M,p}$, and $J_{M,q}$, respectively. Subscript p (q) denotes positively (negatively) charged particles. We expect strong interfacial fields during the steady-state, as sufficient time has passed for screening to occur at the interfaces. To help visualize the interface, Figure 2.2b plots (qualitatively) the expected interfacial E-field profile (black line), illustrating an exponential decay between the electrode surface and the bulk. The corresponding Boltzmann distributions for the positive (red solid line) and negative (blue solid line) particles are also shown. The gradients of these concentration profiles will drive diffusive fluxes. We denote these fluxes as $J_{D,p}$, $J_{D,q}$ for the positive and negative particles, respectively. Diffusion acts on neutral particles as well, so we will also consider the neutral particle diffusive flux $J_{D,n}$. Finally, the field depicted in Figure 2.2b will polarize the nanoparticles and may induce dielectrophoretic motion in the solution. The symbols that we will use for the dielectrophoretic flux of positive, negative, and neutral particles are $J_{DEP,p}$, $J_{DEP,q}$ and $J_{DEP,n}$, respectively. The various particle fluxes, which can only enter the pillbox from solution-side, must total to zero for an ungrowing film:

$$J_{tot} = (J_{M,q} + J_{DEP,q} - J_{D,q}) + (-J_{M,p} + J_{DEP,p} + J_{D,p}) + J_{DEP,n} - J_{D,n} = 0 \quad (2.23)$$

The sign in front of the term indicates the direction of the flux. These signs were determined

with reference to Figures 2.2a and 2.2b. Because we are focused on film-growth (as opposed to dissolution), we use the convention that $+$ $(-)$ denotes inward (outward) flow towards the film (with reference to Figure 2.2a). The individual flux-values themselves (e.g. $J_{DEP,q}$) are positive quantities. The first parenthetical term is the total negative particle flux: $J_q = J_{M,q} + J_{DEP,q} - J_{D,q}$. Likewise, the total positive particle flux is $J_p = -J_{M,p} + J_{DEP,p} + J_{D,p}$. These fluxes oppose each other.

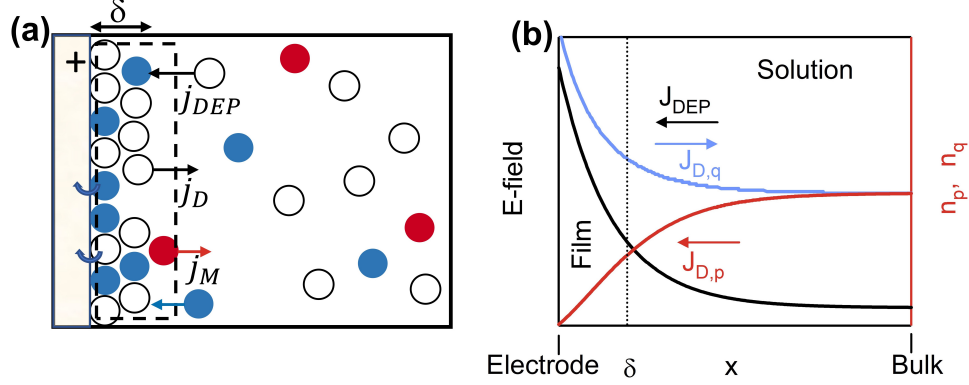


Figure 2.2: (a) Schematic of the steady state period showing the processes contributing to the flux into the pillbox. (b) shows the profiles for E-field (black line), negatively charged particles (blue solid line), and positively charged particles (red solid line) in the interfacial region.

We can simplify Equation 2.23 by considering the steady state current density j_{ss} flowing into the pillbox from the bulk. Expanding j_{ss} in terms of migratory, dielectrophoretic, and diffusive contributions for the positive and negative particle types yields:

$$j_{ss} = (j_{M,q} + j_{DEP,q} - j_{D,q}) + (j_{M,p} - j_{DEP,p} - j_{D,p}) \quad (2.24)$$

The sign convention in Equation 2.24 is the same as discussed above for the early time current density (Eqn. (2.7)). That is, with reference to Figure 2.2a, the rightward flow of positive charge is positive and the leftward flow of negative charge is also positive. All individual current density-values (e.g. $j_{D,q}$) are positive quantities. The first parenthetical term is the total current density due to the negative particles: $j_q = j_{M,q} + j_{DEP,q} - j_{D,q}$, and the total current density due to positive particles is $j_p = j_{M,p} - j_{DEP,p} - j_{D,p}$. These current densities are co-aligned and point rightward. Moreover, they are equal in magnitude;

otherwise, the charge density would evolve at the film surface and the observed current density would not remain constant. Experimentally, we will determine that each charged particle carries a single charge (shown in chapter 4). Here we apply this finding, which allows us to simply convert between flux and current density. Comparing $J_q = J_{M,q} + J_{DEP,q} - J_{D,q}$ to $j_q = j_{M,q} + j_{DEP,q} - j_{D,q}$ allows us to re-write the total negative particle flux as $J_q = j_q/e$. However, comparing $J_p = -J_{M,p} + J_{DEP,p} + J_{D,p}$ to $j_p = j_{M,p} - j_{DEP,p} - j_{D,p}$ indicates that $J_p = -j_p/e$.

Substituting these expressions into Equation 2.23 yields $J_{tot} = \frac{j_q}{e} - \frac{j_p}{e} + J_{DEP,n} - J_{D,n} = 0$. Because j_q and j_p are equal in magnitude, these terms cancel. Thus, Eqn. 2.23 simplifies to

$$J_{DEP,n} - J_{D,n} = 0 \quad (2.25)$$

Hence, we have arrived at a continuity equation for neutral particles in the interfacial region (at steady state). We next use this continuity equation to solve for the steady-state film thickness. The diffusive flux, $J_{D,n}$, of neutral nanocrystal can be written as

$$J_{D,n} = D\nabla n(x), \quad (2.26a)$$

where D and $n(x)$ are the the diffusivity and neutral nanocrystal concentration at position x respectively. The dielectrophoretic flux, $J_{DEP,n}$, for the neutral nanocrystals can be expressed as

$$J_{DEP,n} = \frac{\alpha E(x) \cdot \nabla E(x)}{\zeta} n(x), \quad (2.26b)$$

where α is the nanocrystal polarizability, and ζ is the coefficient of viscous friction ($\zeta = 3\pi\eta d_H$ for spherical particles in solvent of viscosity η). Substituting these expressions for the diffusive and dielectrophoretic fluxes into Eqn. (2.25) yields

$$\nabla n(x) = \frac{\alpha E(x) \cdot \nabla E(x)}{\zeta D} n(x), \quad (2.27)$$

where $\nabla = \frac{d}{dx}$. Equation 2.27 simplifies to

$$\frac{1}{dx} \frac{dn(x)}{dx} = \frac{\alpha}{2\zeta D} \frac{dE^2(x)}{dx}, \quad (2.28)$$

where we have used $\frac{dE^2}{dx} = 2E \frac{dE}{dx}$. Invoking the Stokes-Einstein relation $\zeta D = k_B T$, we obtain

$$\int_{n(x)}^{n_b} \frac{dn(x)}{n(x)} = \frac{\alpha}{2k_B T} \int_{E^2(x)}^{E^2(bulk)} dE^2(x), \quad (2.29)$$

where the bounds of integration are evaluated at position x where $x \geq \delta$ and in the bulk where the neutral particle density is n_b . Equation (2.29) is directly integrated, yielding

$$\ln \frac{n_b}{n(x)} = \frac{\alpha}{2k_B T} (E_b^2 - E^2(x)), \quad (2.30)$$

where $E(b) = B \frac{V}{L}$ is the bulk field. We now need an expression for $E(x)$, the field at the film surface. To estimate $E(x)$, we assume that screening occurs at the interfaces. Applying the theory for electrolytic interfacial screening in conjunction with steady current-flow that was reported in [72], we model the potential in the cell as

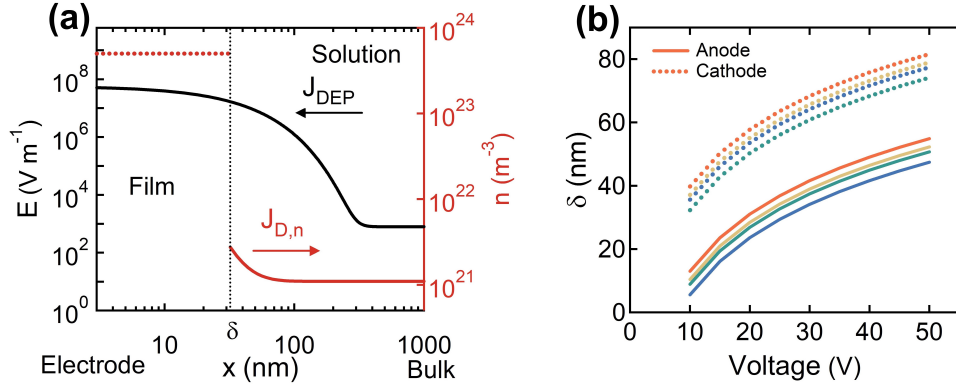


Figure 2.3: (a) Plots of Equation (2.33) for the interfacial field (black solid line) and Equation (2.34a) for the neutral particle concentration (red solid line) as a function of distance from the electrode's surface. The dashed black and red lines represent the bulk field and neutral particle concentration within the film respectively. It also shows the direction of J_{DEP} and $J_{D,n}$. (b) Plot of film thickness (δ) versus applied voltage (V) using realistic values for other parameters in Equations 2.36a (solid lines) and 2.36b (dashed lines). The different line colors denote different neutral nanocrystal concentration in the bulk.

$$V(x) = \frac{V}{2}(-K_1 e^{x/\lambda_{int}} - K_2 e^{-x/\lambda_{int}}) - \frac{VB}{L}x + K_3, \quad (2.31)$$

To determine the coefficients of integration— K_1 , K_2 , and K_3 —we apply the boundary conditions $V(x = 0) = V$, $V(x = L) = 0$, and $V(x = L/2) = \beta V/2$. The quantity β sets the difference between the voltage drops across the anodic and cathodic interfaces and is defined by $\Delta V_{an} - \Delta V_{ca} = (1 - \beta)V$, where ΔV_{an} and ΔV_{ca} are the respective voltage drops. As $|\Delta V_{an} - \Delta V_{ca}|$ cannot exceed $(1 - B)V$, the total interfacial voltage drop, the β is limited by the condition $|1 - \beta| \leq 1 - B$. The three coefficients K_1 , K_2 and K_3 are given by

$$K_1 = \frac{-2 + B + \beta + e^{\frac{L}{2\lambda_{int}}}(-B + \beta)}{(1 + e^{\frac{3L}{2\lambda_{int}}} - e^{\frac{L\lambda_{int}}{2}}(1 + e^{\frac{L}{2\lambda_{int}}}))}, \quad (2.32a)$$

$$K_2 = \frac{(e^{\frac{L}{\lambda_{int}}}(-2e^{\frac{L\lambda_{int}}{2}}(-1 + B) + B - \beta + e^{\frac{L}{\lambda_{int}}}(-2 + B + \beta)))}{((e^{\frac{L}{\lambda_{int}}} - 1)(1 - e^{\frac{L}{2\lambda_{int}}} + e^{\frac{L}{\lambda_{int}}} - e^{\frac{L\lambda_{int}}{2}}))}, \quad (2.32b)$$

$$K_3 = \frac{V(-2e^{\frac{3L}{2\lambda_{int}}} + 2e^{\frac{L\lambda_{int}}{2}} - B - 2Be^{L(\frac{1}{\lambda_{int}} + \frac{\lambda_{int}}{2})} + 2Be^{\frac{L}{2\lambda_{int}}} - \beta + e^{\frac{2L}{\lambda_{int}}}(B + \beta))}{2(-1 + e^{\frac{L}{\lambda_{int}}})(1 - e^{\frac{L}{2\lambda_{int}}} + e^{\frac{L}{\lambda_{int}}} - e^{\frac{L\lambda_{int}}{2}})}, \quad (2.32c)$$

where λ_{int} is an effective screening length associated with the interfacial region. The parameter B is the fraction of applied voltage V that drops across the bulk, L is the length of the cell, and β sets the balance between cathodic and anodic voltage drops. Invoking the general relationship $E(x) = -(dV(x))/dx$, we differentiate Equation 2.31 to obtain the interfacial field profile in the cell:

$$E(x) = \frac{V}{2\lambda_{int}}(K_1 e^{x/\lambda_{int}} - K_2 e^{-x/\lambda_{int}}) + B\frac{V}{L}. \quad (2.33)$$

Figure 2.4 plots Equations 2.31 and 2.33 for the potential and the field, respectively. To visualize these functions across the entire cell, this plot employs an unrealistically large

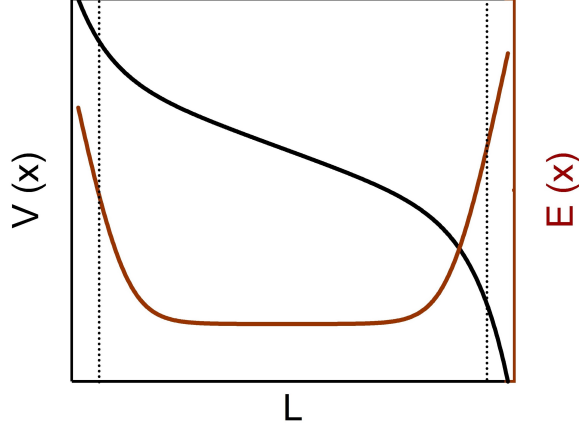


Figure 2.4: Plots of Equations 2.31 (black profile) and 2.33 (red profile) for the potential and the field, respectively, in the entire cell.

screening length of $600 \mu m$, a cell length of $2.0 cm$ and β of 1.1. Near the anode, the coefficients $K_1 \rightarrow 0$ and $K_2 \rightarrow 1$, Equation 2.33 for anodic side simplifies to

$$E_{an}(x) \cong \frac{-V}{2\lambda_{int}} K_2 e^{-x/\lambda_{int}}, \quad (2.34a)$$

where we have neglected $E_b = B_L^V$, a valid approximation when $E_b \ll \frac{-V}{2\lambda_{int}} K_2 e^{-\delta_{an}/\lambda_{int}}$. Likewise, near the cathode, $K_1 \rightarrow 1$ and $K_2 \rightarrow 0$, Equation 2.33 simplifies to

$$E_{ca}(x) \cong \frac{V}{2\lambda_{int}} K_1 e^{\frac{L}{\lambda_{int}}} e^{-x/\lambda_{int}}, \quad (2.34b)$$

where again we have neglected E_b . Using Equation 2.34a, Equation (2.30) results $\ln \frac{n_b}{n(x)} \cong -\frac{\alpha}{2k_B T} \frac{K_2^2 V^2}{4\lambda_{int}^2} e^{-\frac{2x}{\lambda_{int}}}$. Solving for $n(x)$ gives the expression

$$n(x) \cong n_b e^{\frac{\alpha K_2^2 V^2}{8k_B T \lambda_{int}^2} e^{-2x/\lambda_{int}}} \quad (2.35a)$$

At $x = \delta_{an}$, Equation 2.35a becomes,

$$n(\delta_{an}) \cong n_b e^{\frac{\alpha K_2^2 V^2}{8k_B T \lambda_{int}^2} e^{-2\delta_{an}/\lambda_{int}}} \quad (2.35b)$$

Rearrangement yields the film thickness δ_{an} :

$$\delta_{an} \cong \frac{\lambda_{int}}{2} \left[\ln \frac{\alpha K_2^2 V^2}{8k_B T \lambda_{int}^2} - \ln \ln \frac{n(\delta_{an})}{n_b} \right] \quad (2.36a)$$

Similarly, the expression for cathodic film thickness can be written as:

$$\delta_{ca} \cong \frac{\lambda_{int}}{2} \left[\ln \frac{\alpha (e^{\frac{L}{\lambda_{int}}} K_1)^2 V^2}{8k_B T \lambda_{int}^2} - \ln \ln \frac{n(\delta_{ca})}{n_b} \right] \quad (2.36b)$$

Figure 2.3a plots Equation (2.33) (solid black line) for the case of $V = 20 \text{ V}$ and other realistic parameter-values with regard to our experiments ($L = 0.02 \text{ m}$, $B = 0.7$, $\lambda_{int} = 26 \text{ nm}$, and $\beta = 1.1$). This plot illustrates a decay in the E-field by several orders of magnitude between the electrode and the bulk and a commensurate elevation of the neutral particle concentration adjacent to the film-surface. These are the central properties of our system. Additionally, within this model, we see that the approximation $E^2(bulk) \ll E^2(\delta)$ was justified as these values differ by > 6 orders of magnitude in Figure 2.3a. In plotting $E(x) = \frac{V}{2\lambda_{int}}(K_1 e^{x/\lambda_{int}} - K_2 e^{-x/\lambda_{int}}) + B \frac{V}{L}$ across the full interfacial region (film + adjacent solution) in Figure 2.3a, we have assumed that the field is continuous across the film-solution boundary, and we are neglecting screening length-differences between the two media. While not rigorously correct, our approach captures the large magnitude of decay (> 3 orders-of-magnitude) that the E-field must undergo between the film-surface and the bulk. For the sake of providing a semi-quantitative illustration of this important property, we find these assumptions to be acceptable. Figure 2.3a also plots Equation 2.35a for the neutral particle concentration (solid red line). This plot shows an enhancement in the neutral particle density in the region of solution adjacent to the film.

Figure 2.3b plots both anodic and cathodic film thicknesses versus V for a range of n_b values, using a fixed and realistic set of the other parameters α , T , λ_{int} , B , and L . This plot employs $\beta = 1.1$. The film thickens as V increases where as $n(\delta)$ has weaker effect, reflecting its $\ln \ln[n(\delta)]$ dependence.

Chapter 3

Experimental section

3.1 Double Quartz Crystal Microbalance with Amperometry- an innovative tool for thin-film growth

Sauerbery [73] was the first person to envision the usefulness of Quartz Crystal Microbalance (QCM) on sensing the deposited mass on the surface of piezoelectric-device-based QCM electrodes. It consists of a thin quartz crystal disc coated with conducting material on its both surfaces. The entire system is set into oscillation by applying an external electric field between the two electrodes and adjusting the frequency of the applied field close to the resonating frequency of the crystal. The angle at which these crystals are cut controls the various properties of the oscillator: thermal stability, mode of oscillation, resonance frequency, etc. AT-cut crystals being thermally stable are more popular towards this end. Historically, QCM sensors have been used for great deal of scientific studies and their applications continue to grow. In the beginning, they were limited to gaseous media [74]. Recognizing that these sensors could also be used in liquid environments [75], their use has been extended to numerous other applications like electrochemistry [76], biochemistry [77], biomedical [78], polymer science [79], and rheology [80].

Recently, the QCM has gained popularity in real-time monitoring of nanocrystal deposition. QCM has been employed to deposit nanocrystals from both aqueous and organic-based

solvents. Nanocomposite films of polythiophene and metal oxide were deposited on the surface of QCM electrodes from organic-based solvents [81]. In another study, deposition of carbon nanotubes, graphene, and TiO₂ was shown from water-based suspension [82]. Influence of solution chemistry, such as the presence of monovalent or divalent cations and, on the deposition and detachment kinetics of CdTe quantum dots have also been observed [83].

In this thesis, we investigate the electric field-driven assembly of thin films from suspensions of nickel nanocrystals in hexane using a two-electrode double quartz crystal microbalance coupled with amperometry. This approach, novel in the field of EPD, permits quantification of the relationship between a directed flux of nanocrystals and the film growth-rate. This capability enables the determination of important film-growth parameters: nanocrystal charge, the concentrations of the positively and negatively charged nanocrystals, and their initial sticking coefficients. Furthermore, these growth parameters permit estimation of the interfacial field, which we use to predict the terminal film thickness. To quantitatively relate the flux of nanocrystals and the film growth-rate, the mass at both electrodes must be simultaneously measured with the current flowing through the electrodes. To address this need, we have built a double quartz crystal microbalance (QCM), which employs two gold-coated quartz crystals: one for the anode and the other for the cathode.

3.1.1 Design of apparatus

Our purpose-built QCM is shown in Figure 3.1. It consists of a pair of crystal holders, crystals, retainer gears, retainer covers, and a single piece of the cylindrical tube. We replaced the retainer holder that comes with the standard Stanford Research Systems QCM assembly with the locking-ring assembly as shown in the figure. We assembled them in the order of crystal holder, crystal, retainer gear, and retainer cover. The retainer gear whose other end is threaded externally holds the QCM sensor in place in the QCM holder. The retainer cover helps to stabilize the gear. We connect the identically assembled QCM-1 and QCM-2 using the Teflon cylinder, which is threaded internally.

Our final setup is shown in the figure 3.2. The sample cell employed a quartz crystal

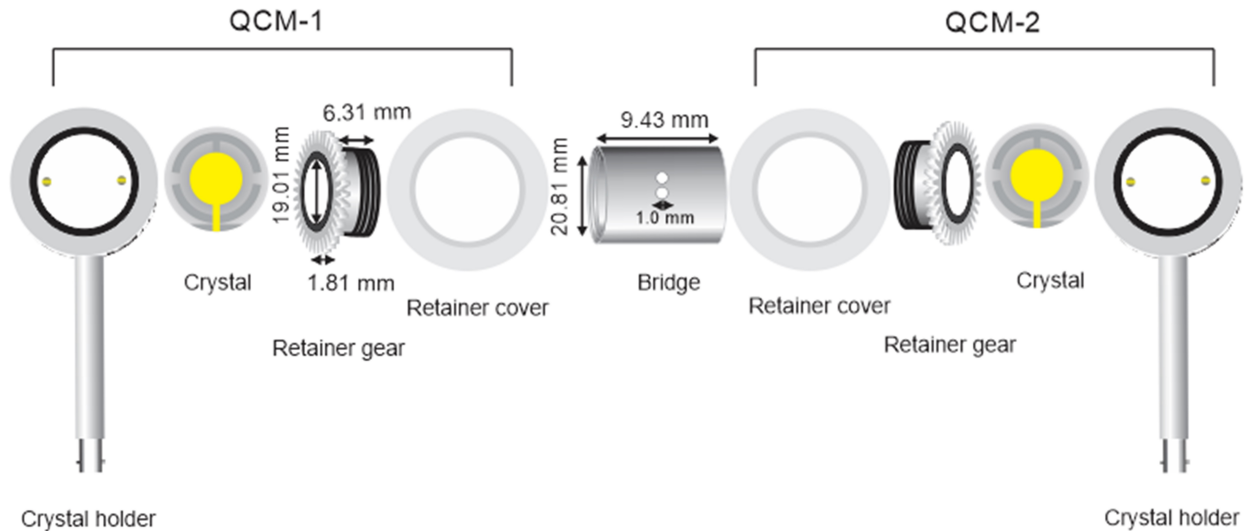


Figure 3.1: *Crystal holder and components.*

microbalance (QCM) plate for both the working electrode (WE) and counter-electrode (CE). We maintain a WE-CE separation of 20.4 mm or 30.03 mm depending on the tube-length. The total volume of the cell was 6.0 mL or 9.0 mL. Prior to use, we plasma cleaned each plate, filled the cell with the nanoparticle suspension, and calibrated each sensor. The primary capability of this approach is to observe the electrical current density $j(t)$ and the deposited masses in response to the application of a step-function voltage signal at time-zero. We have written a Python code to automate the voltage-application and data-acquisition steps. This process entails controlling a source-meter (Keithley 2400) both to bias the WE (while grounding the CE) and to measure the current density, and digital controllers (Stanford, QCM200) to measure the frequency shifts Δf of each sensor. We employed the Saurbrey equation $\Delta m = (6.99 \times 10^{-9} \frac{g}{Hz}) \Delta f$ to convert frequency shift Δf to deposited mass Δm .

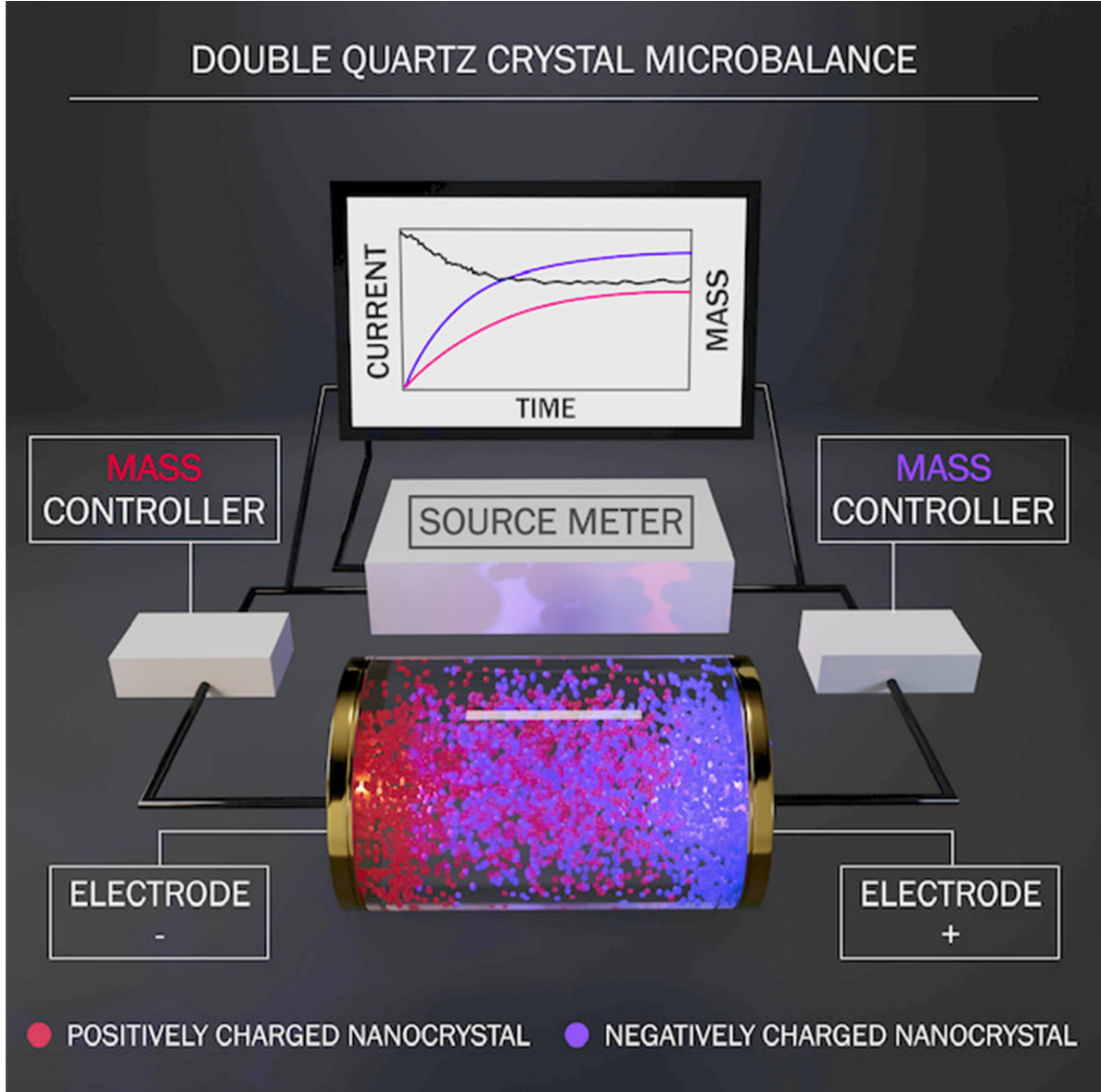


Figure 3.2: Double quartz crystal microbalance setup to measure mass at each electrode and current simultaneously.

3.1.2 Calibration of QCM in Hexane

AT-cut gold-coated quartz crystal (5 MHz) having active electrode are of $\sim 0.4 \text{ cm}^2$ was used for the mass measurement. The shift in frequency of the crystal due to the addition of mass is given by Saurebrey equation [73].

$$\Delta f = -C_f \Delta m, \quad (3.1)$$

where Δf is the frequency shift (Hz) of the crystal due to deposited mass, C_f is the calibration constant (Hzg^{-1}), and Δm is the deposited mass (g).

In our study, we used quartz a crystal microbalance to measure the deposited mass in real-time. However, our first measured quantity was the frequency shift, Δf , of the quartz crystal microbalance. To convert frequency shift to the deposited mass, we used Equation 3.1. In order to use Equation 3.1 to get the mass, we need the calibration constant, C_f . For this, we calibrated the QCM prior to use for the nanocrystal deposition.

The protocol for calibrating the quartz crystal was as follows. First, the frequency of the unloaded crystal (f_1) was determined in hexane. Second, a known mass of silver was deposited galvanostatically from an aqueous solution. Third, the frequency of loaded crystal (f_2) was determined in hexane. The frequency shift of crystal in hexane due to the known mass of silver is given by $\Delta f_{Ag} = f_2 - f_1$. Finally, the calibration constant, C_f is found from the Sauerbrey equation (Eqn. 3.1), as described next.

In more detail, a known mass was deposited on the QCM crystal by galvanostatic electrodeposition of silver from the aqueous solution of 5 *mM* AgNO_3 and 200 *mM* KNO_3 at room temperature [84]. For silver deposition, a three-electrode electrochemical cell was used with the QCM crystal as a working electrode (WE), silver wire as a reference electrode (RE), and gold plate as a counter electrode (CE). The current density used in this study was 500 $\mu\text{A cm}^{-2}$. In Figure 3.3, the black profile represents the frequency shift of crystal as a function of time during silver electro-deposition and red profile is the current applied during the period of deposition (~ 1200 s).



The amount of silver deposited on the crystal (Δm_{Ag}) as determined from the current was calculated using

$$\Delta m_{Ag} = \frac{AW_{Ag} \times \Delta Q}{zF}. \quad (3.3)$$

where $\Delta Q = It$ is the charge involved in electrodeposition of silver, I the applied current, t the deposition time, AW_{Ag} the atomic weight of silver (107.87 *g/mol*), $z = 1$ the charge for

silver ions, and F the faraday constant (96485.33 C/mol).

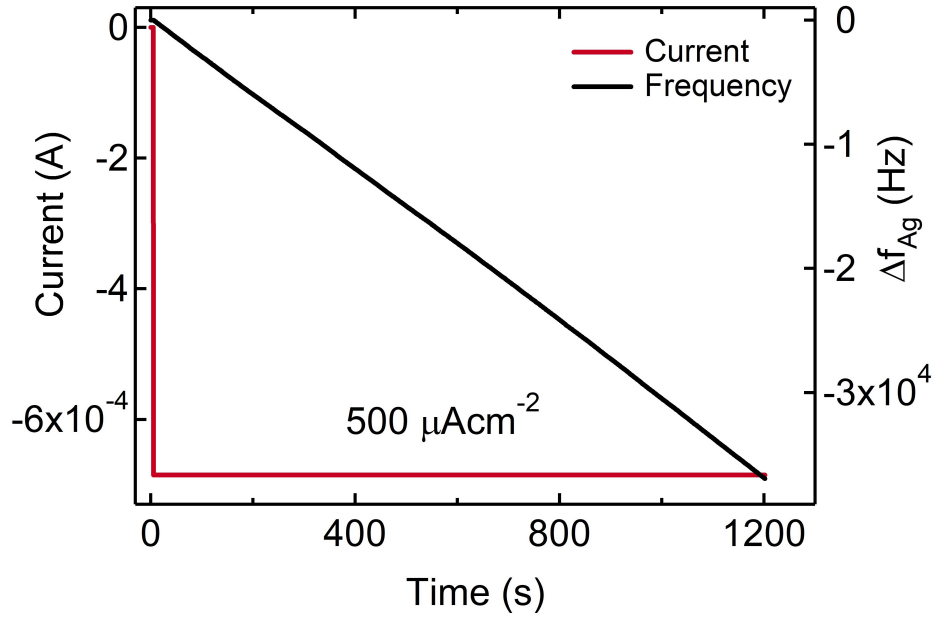


Figure 3.3: Shift in frequency as a function of time during electrodeposition of silver from a 5mM aqueous silver nitrate solution (black) and the applied current pulse (red).

To account for the viscous loading of the solvent, the QCM must be calibrated with respect to hexane. We made this correction by measuring the frequency of QCM crystal in hexane before (Figure 3.4a) and after (Figure 3.4b) mass loading. Figures 3.4a and 3.4b show that the frequency of the unloaded crystal in hexane was $f_1 = 5006710 \text{ Hz}$ and that of silver loaded crystal was $f_2 = 4968760 \text{ Hz}$. The difference $f_2 - f_1$ gave the frequency shift of the silver-loaded crystal, Δf_{Ag} , in hexane.

After knowing the amount of silver in the crystal (Δm_{Ag}) and the corresponding shift in frequency in hexane (Δf_{Ag}), we calculated the calibration constant, C_f , of the crystal by employing the relation:

$$C_f = \frac{-\Delta f_{Ag}}{\Delta m_{Ag}}. \quad (3.4)$$

Figure 3.5 plots the values of C_f determined for seven different QCM crystals used for the electrodeposition of nickel nanocrystals during EPD. The average and standard deviation of C_f are $1.43 \times 10^8 \pm 0.06 \times 10^8 \text{ Hz/s}$.

Having determined C_f , we convert the measured frequency shifts (Δf) due to Nickel

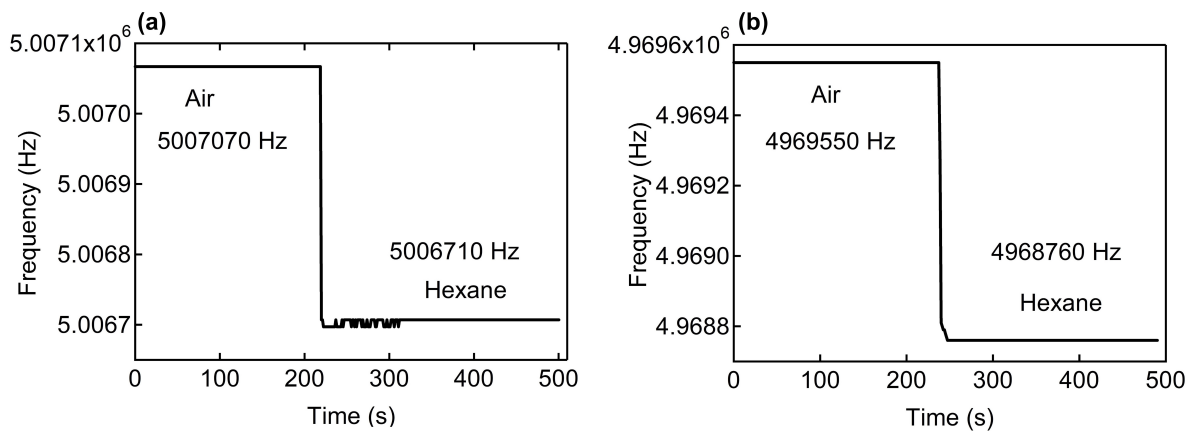


Figure 3.4: Frequency profile of crystal when taken from air to hexane before (a) and after (b) the silver was loaded on the crystal.

nanocrystal deposition into mass by employing the relation: $m = (6.99 \times 10^{-9})\Delta f(g)$ using the known active area of the QCM.

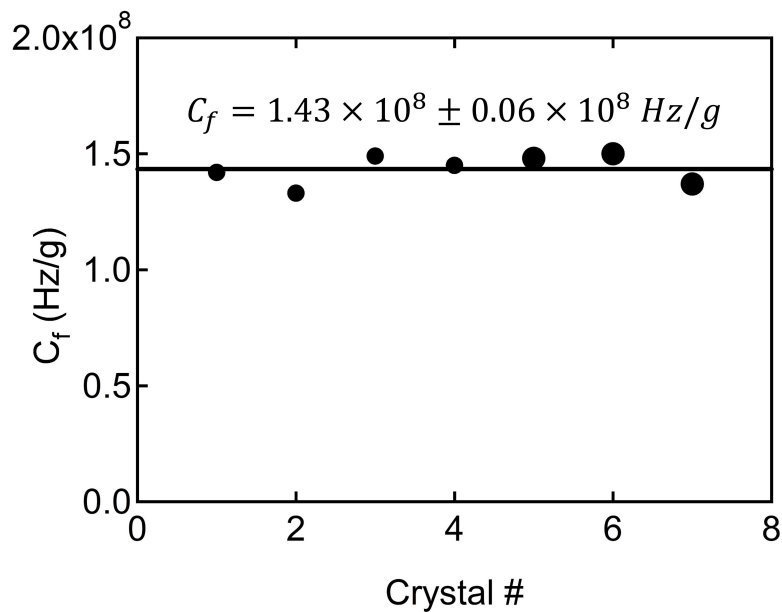


Figure 3.5: Calibration constant calculated for different crystals in Hexane.

3.2 Nickel Nanocrystal Synthesis and Cleaning

Nickle (Ni) nanocrystals are synthesized using a published procedure [85]. In a typical synthesis, 26.75 g of oleylamine (Aldrich, 70% technical grade) in a 100 ml round bottom flask is degassed while stirring for ~ 1 hour on a Schlenk line at 80°C . To this 1.285 g of nickel acetylacetonate (95%, Aldrich) is added under nitrogen and slowly degassed by iteratively switching between nitrogen and vacuum. Once degassed, 4.46 ml of tri-n-octylphosphine (90%, Alfa Aesar) is injected and the solution is heated to 220°C in ~ 20 minutes and then held for 2 hours under a nitrogen environment while continually stirring with a magnetic stir bar. A long condenser tube is used to separate the round bottom flask from the manifold to prevent splashing associated with the decomposition of the nickel acetylacetonate. The final solution has mole ratios of 1:2:20 nickel acetylacetonate: tri-n-octylphosphine: oleylamine. The solution is then cooled (under nitrogen) to room temperature using a water bath. The mole ratios were varied to adjust nanocrystal size as indicated by Carenco *et al.*

To clean, the nanocrystal solution is centrifuged at 8000 rpm for 5 min using $\sim 1.5\times$ volume of acetone as an anti-solvent. The precipitated pellet, containing oleylamine capped nickel nanocrystals, is dispersed in 4 ml hexane. To exchange ligands from oleylamine to oleic acid an excess of oleic acid ($\sim 0.1\text{ M}$) is added to the nanocrystal-hexane solution, sonicated, and then reprecipitated by adding 11ml acetone ($\sim 3\times$) and centrifuging for 5 minutes at 8000 rpm. The ligand exchange process is repeated twice. Final solutions are dispersed in 10 ml hexane with one drop of oleic acid and are typically stable for months.

The final cleaning prior to use in deposition experiments is similar to that described above but excess ligand is not added. Deposition was measured as a function of 1-5 cleaning cycles and found not to change after two cleaning cycles. Thus, two final cleaning cycles were used for most experiments. After cleaning, mass was determined for each batch by placing a known volume into a tared vial and weighing after the solvent was evaporated.

3.3 Small Angle X-ray Scattering Measurements to Determine Nanocrystal Size

Small angle X-ray scattering (SAXS) measurements were performed at the Advanced Light Source on beamline 7.3.3 using an X-ray wavelength of 1.24 Å, a beam size of approximately $1 \times 0.8 \text{ mm}$ at the sample, and a sample to detector distance that varied from 2 to 2.4 m [86]. Scattering photons were collected using a Pilatus 2M detector with 1475×1679 pixels and a pixel size of $172 \mu\text{m} \times 172 \mu\text{m}$. Scatter angles were converted to wavenumbers (q) using silver behenate as a calibrant. Data was processed using the Nika [87] and Irena [88] software packages written by Jan Ilavsky and run under Igor Pro software (WaveMetrics, Inc).

To determine nanocrystal diameters and distributions from SAXS, solutions of $\sim 1 \text{ mg/ml}$ nickel nanocrystals dispersed in hexane were placed in 2 – 2.5 mm quartz thin-walled capillary tubes (Charles Supper, Westborough, MA) and compared with a hexane background. Scatter plots were typically collected for 60 – 120 s. Two-dimensional data was circularly integrated and normalized by the incident flux and the collection time. The nanocrystal size distributions were calculated assuming a Gaussian distribution of non-interacting spheres. The scatter intensity is given by [89]

$$I(q) \propto \int_0^\infty N(R)P(qR)R^6 dR, \quad (3.5)$$

where q is the scatter vector, R is the nanocrystal radius, $N(R)$ is the nanocrystal size distribution and $P(qR)$ is the form factor. We assume a Gaussian size distribution given by

$$N(R) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left[-\frac{(R - \bar{R})^2}{2\sigma^2}\right], \quad (3.6)$$

where $\bar{R}$ is the average radius and σ is the standard deviation. The form factor $P(qR)$ for homogenous spheres is

$$P(qR) = \left[3 \frac{\sin(qR) - qR \cos(qR)}{(qR)^3}\right]^2 \quad (3.7)$$

Combining Equations 3.5-3.7 allowed us to fit background-subtracted Porod plots to find the average diameter $\bar{d} = 2\bar{R}$ and the Gaussian width $\delta = 2\sigma$. The mean nanocrystal diameters for the 7 batches studied are summarized in Table A.2.

Table 3.1: *Nickel nanocrystal diameter*

Batch	1	2	3	4	5	6	7
$d \text{ (nm)}$	9.9	11.0	11.0	12.5	13.0	13.5	16.1
$\sigma \text{ (nm)}$	1.1	1.0	1.0	1.1	1.0	1.0	1.1

3.4 Conversion Relations for Nanocrystals Number and Film Thickness

In this study, we correlate mass transfer and charge transfer kinetics at early time to quantify the important growth parameters. We will do so (shown in chapter 4) by comparing the growth rate of the film to the particle flux. For this analysis, we need the number of nanocrystals deposited in the film. At long time, we use steady-state values for mass and current to estimate the interfacial field. We use this interfacial field to predict the film thickness in terms of process parameters: applied voltage and nanocrystal concentration. For this analysis, we need to convert nanocrystal numbers into film thicknesses. In this section, we present the relations used to convert the deposited mass into the number of nanocrystals and the film thickness.

3.4.1 Conversion of Mass into Number of Nanocrystals

The number of nanocrystals (N) deposited on each electrode is determined from the known deposited mass, m , by using the relation:

$$N = \frac{m}{\rho_{np} V_{np}}, \quad (3.8)$$

where ρ_{np} and V_{np} are respectively density and volume of each nanocrystal and given by relations $\rho_{np} = \frac{\rho_{oleic}(d_H^3 - d^3) + \rho_{np}d^3}{d_H^3}$, $V_{np} = \frac{\pi d_H^3}{6}$, where $\rho_{oleic} = 8.95 \times 10^{-1} \text{ g/cm}^3$ is the density of oleic acid, $\rho_{np} = 8.91 \text{ g/cm}^3$ is the density of nickel core, d_H is the hydrodynamic diameter of nanocrystals, and d is the measured core diameter of nanocrystals. We assumed oleic acid ligands contributed a 2 nm thick shell to the nanocrystals.

3.4.2 Conversion of Number of Nanocrystals into Film Thickness

The film thickness (δ) on each electrode is determined from the number of nanocrystals deposited on electrodes as follows: We approximate the monolayers by assuming a close-packed hexagonal array of nanocrystals (Figure 3.6a). We first calculate the number of nanocrystals required to form a monolayer.

$N_{ml} = \frac{\text{Area of electrode}}{\text{Area of hexagon}}$ (number of nanocrystals in one hexagon) From Figure 3.6b, the number of nanocrystals in one hexagon is 3. so, $N_{ml} = \frac{A}{3\sqrt{3}d_H^2/2} \times 3$, where d_H is the center to center distance also known as lattice constant and A is the electrode area.

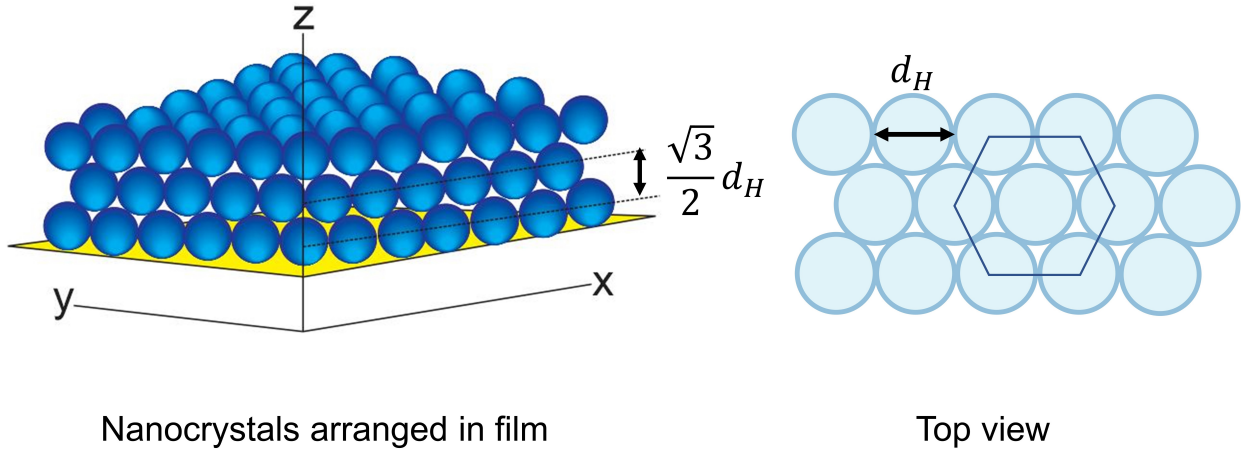


Figure 3.6: (a) Close-packed hexagonal array of nanocrystals. (b) Top view.

Then, the film thickness (δ) can be written as

$$\delta = \frac{\sqrt{3}N}{2N_{ml}}d_H, \quad (3.9)$$

where $\sqrt{3}/2d_H$ is center to center distance between two adjacent monolayers.

Chapter 4

Nanocrystal Film Deposition from Non-Aqueous Suspensions

4.1 Abstract

This study presents a novel method to correlate the mass and charge transfer kinetics during the electrophoretic deposition of nanocrystal films by using a purpose-built double quartz crystal microbalance combined with simultaneous current-measurement. Our data support a multistep process for film formation: generation of charged nanocrystal flux, neutralization via charge transfer at the electrode, and polarization of neutral nanocrystals near the electrode surface. The neutralized particles are then subject to dielectrophoretic forces that reduce diffusion away from the interface, generating a sufficiently high neutral particle concentration at the interface to form a film. The correlation of mass and charge transfer enables quantification of the nanocrystal charge, the fraction of charged nanocrystals, and the initial sticking coefficient of the particles. These quantities permit calculation of the film thickness, providing a theoretical basis for using concentration and voltage as process parameters to grow films of targeted thicknesses.

4.2 Introduction

Our reliance on optoelectronic devices drives a growing demand for technological thin films that will enable large-area, flexible electronics [11; 12]. In this venue, colloidal nanoparticles are promising building blocks [90–93]. Recent work has exploited their diversity of shape, size, and ligand-tunable functionality to self-assemble films with complex, superlattice architectures and emergent functionalities that are of potential use in electronic, photovoltaic, and sensing applications [13–15]. In fact, the range of superlattices that researchers can now synthesize numbers in the hundreds [94–102]. That said, most nanocrystal superlattice-systems have yet to be employed in manufactured devices. The formation of nanocrystalline films is reliant on solution-phase processing, which has the attributes of being low-cost, low-temperature, and in some cases, green [103; 104], but which lag behind vapor phase methods, which are manufacturing workhorses [105; 106], in terms of the degree of control over the films that they provide. Solvent evaporation [107–109], spin coating, dip coating [110; 111], and layer-by-layer self-assembly [112; 113] are methods for growing nanocrystal superlattices that see wide use—enabling, the production of deformable conductive films [114] and methods for particle-deposition onto curved substrates [112; 115]. However, these methods lack direct control over the particle-flux during film-growth. Flux control is important as it is needed to quantify how films grow and to identify key factors of the growth process(es). More detailed quantification of solution-phase growth processes will permit better understanding and control of the deposition processes by suggesting which interface processes are most important and, thereby, enable more reliable assembly of nanoparticle films.

The use of electric fields to control nanocrystal flux during film-growth is an attractive concept as it provides a means to direct the flux of building blocks onto a specified substrate and is potentially integrable into multi-step processing [116; 117]. Work over the past two decades has demonstrated field-induced film-formation in many nanocrystal-systems [53–64; 66–70; 118–120]. It was recently shown that electric field assisted deposition can produce nanocrystal superlattices with long-range 3D order [121]. Researchers have also observed the expected proportionality between the thickness of deposited films and the primary pa-

rameters of the growth-process, initiating a basis for controlling film-growth. For example, by measuring the current-voltage response during film-growth, the total charge that flows during E-field-assisted deposition was found to correlate with final film thickness [71]; additionally, the film-mass was found to scale with reasonable collective variables, involving particle concentration and electric field [122]. These findings relied on analysis of the films after the growth process took place. Therefore, researchers have since quantified the field-driven nanoparticle flux *during* the growth of the film, employing x-ray diffraction to detect the interfacial nanocrystal concentration during superlattice-formation [123]. The observed linear relationship between the flux and the applied field established the electrophoretic nature of the flux and demonstrated its efficacy over superlattice nucleation density on the substrate. However, there have been few studies of electric field driven superlattice assembly that couple the *in situ* detection of film growth with electrochemical techniques to correlate mass transfer with electron transfer. Such investigation is needed to advance our understanding to the point where we can make accurate predictions of the properties of a film, such as growth rate and thickness, based on the process-parameters of the system, such as particle concentration, applied voltage, and time.

A key challenge in this regard is that even for a simple solution composed of a single nanocrystal type, the particles may carry different amounts of charge. The growth rate in this case may still be linearly proportional to the field, which is desirable, but the slope of this response will have a complex dependence on the solution properties and may be difficult to adjust, limiting the realizable range of growth-rate. Generally, quantitative EPD requires knowledge of the number of charged species, the charge of each species, their individual concentrations, and their individual sticking coefficients. A sticking coefficient is defined as the ratio of the attaching particle-flux to the incident particle-flux on the film. One generally needs a commensurate number of measurements to quantify these properties. Laser Doppler velocimetry [118; 124] can provide the charge of the particles but is less effective for suspensions of oppositely charged particles (due to cancellation of the Doppler shifts) and for optically opaque solutions (as is the case for many nanocrystal solutions). In thermally charged nanocrystal populations, which are common [125], the nanocrystal suspensions re-

tain a sizeable fraction of neutral particles, so the total particle concentration, which is straight-forward to measure, does not determine the charged particle concentration. While recent work has demonstrated the selective placement [126], and the controlled deposition [127] of nanocrystals using EPD [121; 123; 128–134], these achievements have been made despite incomplete knowledge of the particle-level properties discussed above. Moreover, while assuming sticking coefficients of unity and univalent charges on the nanocrystals may be reasonable in specific cases [135], determining the charged fractions of the nanocrystals is still an outstanding problem [136]. Therefore, in this study we employ for the first time (to our best knowledge) a complement of three *in situ* measurements to monitor cathodic and anodic nanocrystal film-growth rates and current density, in real time. This capability permits determination of the sticking coefficients, the particle charges, and the fractions of particles that are charged in a thermally charged, electrolyte where the nanocrystals are the only charge carriers. This quantitative analysis permits the theoretical prediction of the terminal thickness of the films.

4.3 Experimental methods

In this study, we investigate the field-driven assembly of $\sim 50\text{ nm}$ thick amorphous films from the suspension of nickel nanocrystals in hexane using a two-electrode double quartz crystal microbalance (QCM) coupled with amperometry. This approach, novel in the field of EPD, permits correlation of the *mass* transfer kinetics with the overall *charge* transfer kinetics. Here we show that by correlating the mass and charge transfer kinetics, we determine the nanocrystal charges, the concentrations of the positively and negatively charged nanocrystals, and their initial sticking coefficients. In turn, this analysis elucidates an interfacial-field based mechanism for film-growth such that once the nanocrystals are neutralized, they are held near the electrode (in a region defined by the screening length) due to dielectrophoretic forces. This allows a concentration of neutral nanocrystals to build up at the electrode interface.

To quantitatively relate the mass transfer and charge transfer kinetics, the mass at both

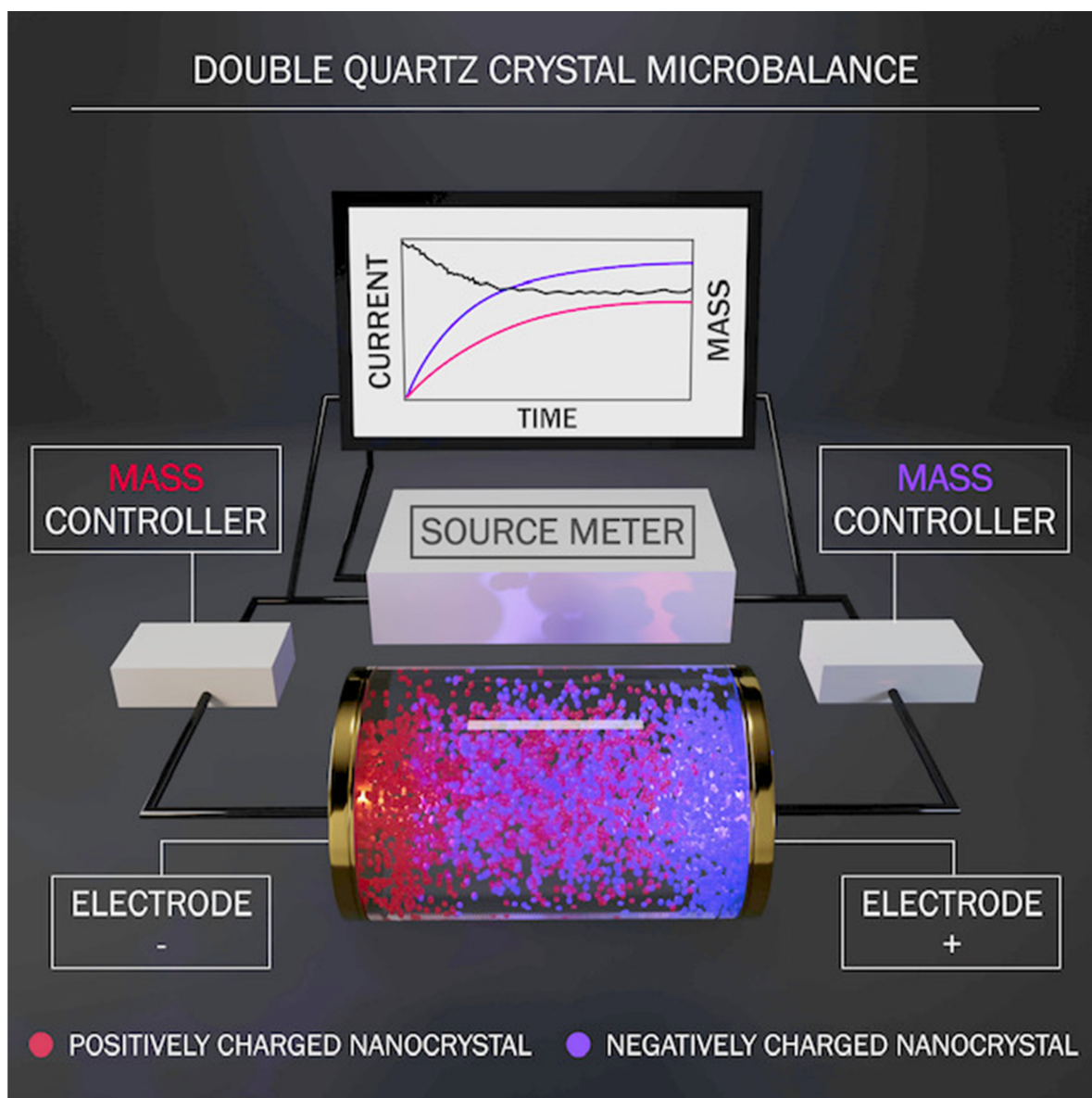


Figure 4.1: *Double quartz crystal microbalance system enables simultaneous measurement of the current and the mass at each electrode.*

electrodes must be simultaneously correlated with the current flowing through the electrodes. To address this need, we have built a double quartz crystal microbalance (QCM), which employs two gold-coated quartz crystals: one for the anode and the other for the cathode (Figure 4.1). A voltage across the anode and cathode generates an electric field within the suspension that drives positive nanocrystals to the cathode and negative nanocrystals to the anode. In a typical experiment, the particle flux is measured as a current and the mass of

film that builds up on each electrode is measured as a frequency shift (Figure 4.1).

The sample cell was fabricated using a locking-ring assembly (Figure 3.1) to hold QCM crystals in place and a teflon tube to connect the two QCM crystal holders (Stanford Research Systems), thereby maintaining a distance of 20.35 *mm* or 30.03 *mm* between the electrodes. The total volume of the cell was 6.0 *ml* or 9.0 *ml*, depending on the tube length. Prior to use, we plasma cleaned each plate and filled the cell with the nanocrystal suspension. The method for calibrating the QCM sensor is described in Chapter 2. The primary method used within this paper was to observe the electrical current density $j(t)$ and deposited masses on both electrodes in response to the application of a voltage-step at time-zero. To this end, a Python code set the electrode bias and measured the corresponding current density via a source meter (Keithley 2400), and simultaneously measured the frequency shifts Δf of each sensor, via a digital controller (Stanford, QCM200), thereby automating the data-acquisition. We employed the Saurbrey equation $\Delta m = (6.99 \times 10^{-9} \frac{g}{Hz}) \Delta f$ to convert the frequency shift Δf to deposited mass Δm (Chapter 2). The time resolution of the data-acquisition process was 0.18 *s*. The uncertainty in our $j(t)$ and Δf measurements was $\pm 0.4 \frac{\mu A}{m^2}$ and ± 1.0 *Hz*, respectively.

This study investigated 7 batches of oleic acid capped nickel nanocrystals. The bulk particle concentrations c_b were varied from 3 *mg/ml* to 30 *mg/ml* and had mean particle diameters, d_H , that ranged between 13.9 and 20.1 *nm* as measured by small angle X-ray scattering. See Chapter 2 for details on nanocrystal synthesis, size determination, and concentration calculations.

4.4 Results

This section is divided into two sub-sections. The first sub-section discusses the early time period (< 1 *s*) where we present the method to determine the major film-growth parameters: charge on the nanocrystal, fractions of charged nanocrystals, and initial sticking coefficients. In the next sub-section, we use the steady-state current and mass data to estimate the interfacial field which we use to predict the terminal film thickness in terms of applied

voltage and nanocrystal concentration.

4.4.1 Early time period

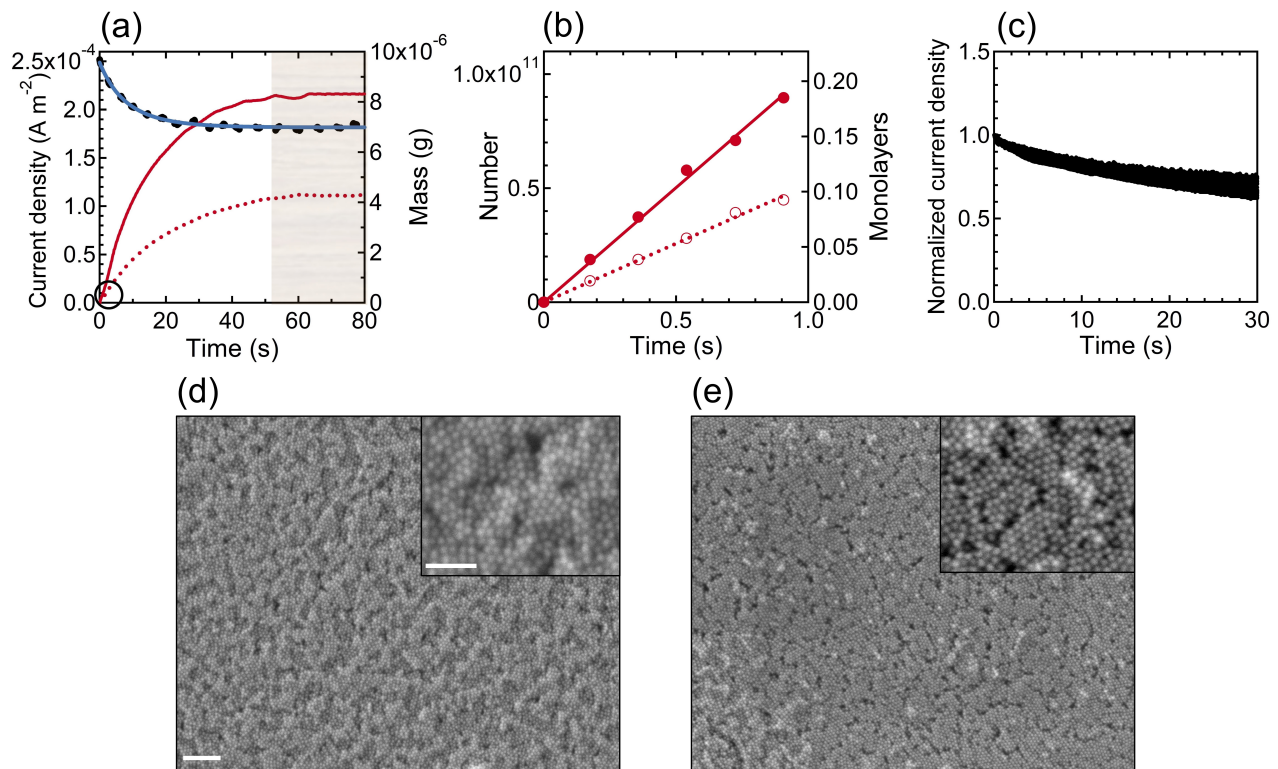


Figure 4.2: Representative raw data and films. **(a)** Current density profile (black filled circles) for a voltage-step of 33.0 V and an electrode spacing of ~ 20 mm. The blue line is a bi-exponential fit to the data. The solid (dashed) red line is the simultaneously collected mass that was deposited on the anode (cathode). The circle indicates the early time region re-plotted in **(b)**. The shaded region indicates the steady-state regime. **(b)** Number of particles (left axis) and monolayers (right axis) deposited on the anode (red solid) and cathode (red open) during the first 0.9 s of voltage-step measurement as determined by mass change. The lines are the linear fits to the data-sets. **(c)** Normalized current density, $(j(t))/j_0$, profiles for 45 different trials. **(d)** and **(e)** are scanning electron micrographs of the cathode and anode, respectively following voltage-step experiments. Scale bar = 200 nm. Insets: enlarged view of the films. Scale bar = 100 nm.

Typical data (Figure 4.2a) consist of the time evolution of three curves: the current density (filled circles), the anode mass-change (solid red line), and the cathode mass-change (dashed red line). These measurements permit the mass at both electrodes or equivalently the total number of deposited nanocrystals to be quantitatively correlated with the number

of electrons transferred to the electrodes as a function of time. In this particular example, a voltage step of $V = 33.0 \text{ V}$ caused $8 \mu\text{g}$ to be deposited on the anode and $4 \mu\text{g}$ on the cathode over $\sim 50 \text{ s}$ period. Beyond 50 s , the masses remained essentially constant, indicating that film-growth slows to a stop during a typical voltage step experiment. Below we refer to this period as the steady-state region. Such monotonic and sublinear profiles are typical of our results. This figure also shows that the corresponding current density (filled black circles) decays bi-exponentially during film formation and reaches a steady value with a time constant similar to the mass profiles. Experimental control studies without nanocrystals (pure hexane and hexane-oleic acid solutions) exhibited negligible mass changes and current density during the voltage-step experiments (Appendix A) whereas suspensions with nanocrystals led to film formation on both electrodes. These observations indicate that the nanocrystals serve as both the positive and negative charge carriers as well as the depositing species. The early time region encircled in Figure 4.2a is expanded in Figure 4.2b. It shows that during the first second of deposition the deposited nanocrystal number/monolayer increases linearly with time as indicated by linear least square fitting ($R^2 = 0.99$) to the data. Furthermore, the current density in all investigated samples, which varied significantly in particle concentration and applied voltage, exhibited the same decay kinetics (Figure 4.2c) as the plot of normalized current densities, $\frac{j(t)}{j_0}$, for 45 different trials. Figures 4.2d and 4.2e are the SEM micrographs of films deposited at cathode and anode respectively. The insets depict the polycrystalline nature of these films. See *ex situ* characterization of the nanocrystal films in Appendix A for details.

We break up our analysis of these mass and current data into the early time response ($t < 1 \text{ s}$) when the electric field can be approximated as the applied field (Figure 4.3a) and the steady state response ($t > 42 \text{ s}$) when the film has stopped growing but current continues to flow (Figure 4.3b). At early times we first establish a relationship between the growth rates (as determined by the mass) and the electron transfer (as determined from the current). These data sets are then used to quantify the charge per nanocrystal (z), the early time sticking coefficient ($s(0)$), and the fraction of charged nanocrystals (f). We then use the steady state mass and current values to quantify the electric field across

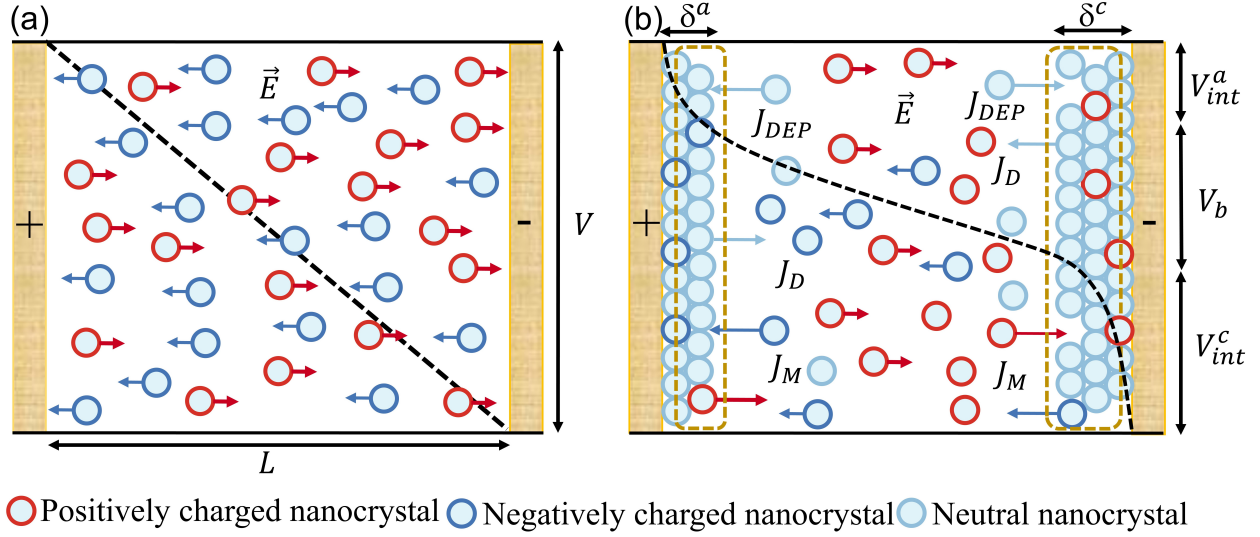


Figure 4.3: Schematic of EPD process. (a) Depiction of the early time period when the nanocrystals drift towards the electrodes of opposite polarity after the electric field is applied. The dashed line shows the potential profile across the cell. (b) Depiction of the steady state regime showing different processes contributing to the total flux into the pillbox (dashed yellow rectangle). The schematic shows the establishment of the screening layers, the formation of neutral nanocrystals via charge transfer with electrodes, and the profile of the cell potential (dashed black line). The film forms predominantly from neutral nanocrystals that are held near the electrode surfaces due to dielectrophoretic forces associated with the field and field gradient.

the electrode interface (E_{int}) and use this to estimate the polarization of the nanocrystals within the interface and the corresponding dielectrophoretic forces on them. Together these measures establish a relationship between film thickness (δ) and process parameters such as bulk concentration (c_b) and applied voltage (V).

The mass measures the number of nanocrystals (N) that join each electrode. In particular, at early times before the double layer is established, the mass response shows that the number of particles that attach to the electrodes is linear with time (exemplary data shown in Figure 4.2b). This allows us to extract the initial growth rate, ($\dot{N}_0$), as the slope of the nanocrystal number versus time plot. The slopes-values were found using linear least squares fitting of the data, constrained to have y-intercepts of zero. These determinations have uncertainties of $\pm 2 \times 10^9 \frac{\text{particles}}{\text{s}}$. Data fits were made for 89 samples which differed in initial field strength, particle concentration, and particle size. These variations allowed

us to vary the flux and hence the growth rate over approximately ~ 2 orders of magnitude; the growth rate of particles depositing on the cathode, for example, ranges from 5×10^9 to $2 \times 10^{11} \text{ s}^{-1}$. Figures 4.4a and 4.4b compile the growth rates as a function of applied electric field ($E_0 = V/L$) at the cathode and anode respectively, where the different symbol-colors denote different nanocrystal-batches and/or concentrations.

These data can be further evaluated by noting that the number of depositing particles per unit time (normalized by the electrode area, A) is equal to the particle flux times the sticking coefficient where the particle flux is given by the product of the particle concentration and the particle velocity. For a single species p of positively charged nanocrystal that deposits on the cathode, we re-write Equation (2.11b)

$$\frac{\dot{N}_0^{cathode}}{A} = \frac{e}{3\pi\nu d_H} (s_p(0) f_p z_p) c_b E_0, \quad (4.1)$$

where $s_p(0)$ is the sticking coefficient of the positive species p , f_p denotes the fraction of positively charged particles, z_p the charge per nanocrystal, and c_b the bulk nanocrystal concentration. The growth rate at the anode has a similar form except with negatively charged nanocrystals. As suggested by Equation 4.1, all of the mass data collapse to a line when the normalized growth rate is plotted against $e/(3\pi\nu d_H) c_b E_0$. Using linear least-squares fitting, these plots (Figures 4.4c and 4.4d) reveal a slope ($s_p(0) f_p z_p$) of 0.18 and a slope ($s_q(0) f_q |z_q|$) of 0.20 for the positive and negative nanocrystals respectively. The uncertainty in these slope-determinations (± 0.03) is primarily due to the 10% polydispersity in the particle size.

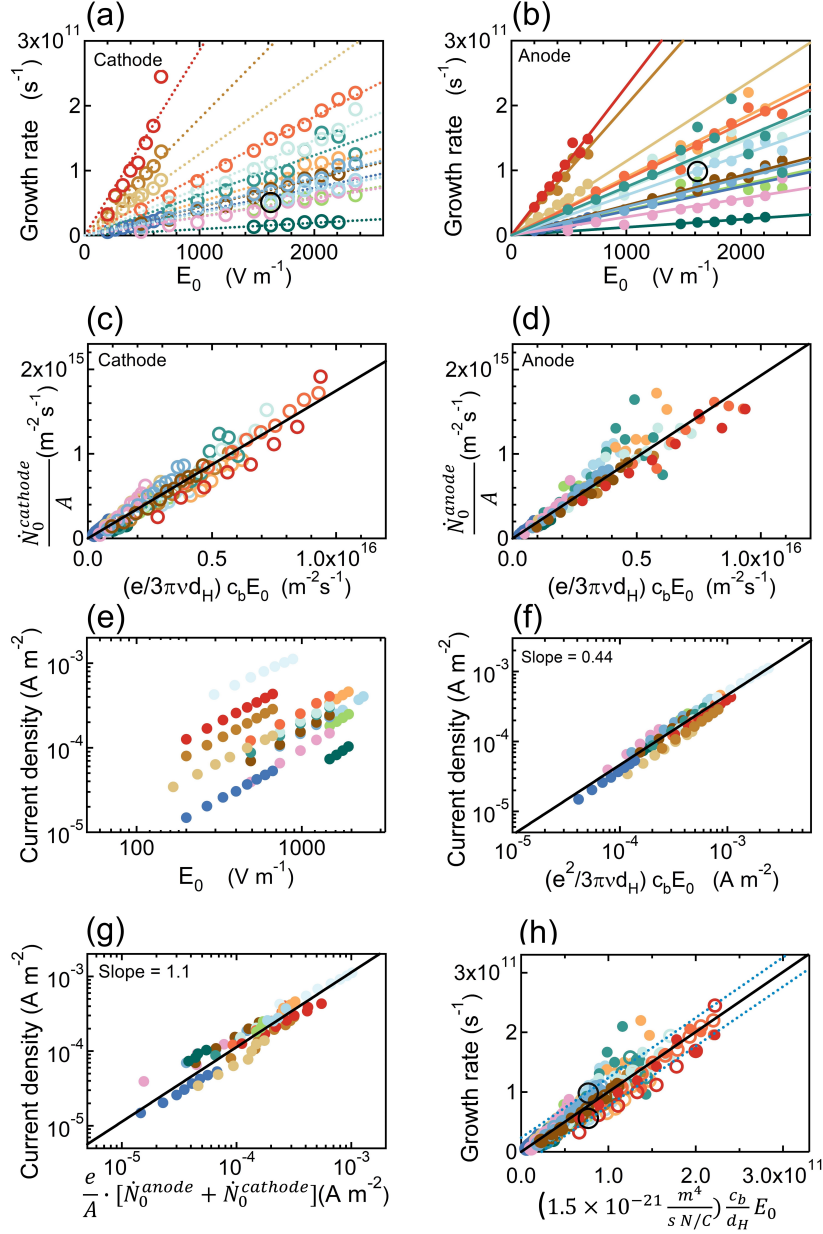


Figure 4.4: Growth rate versus applied electric field E_0 for positive (a) and negative (b) nanocrystals. The black circle in each panel identifies the data point from figure 4.2b. The dashed lines are linear least squares fits to the data, constrained to pass through the origin. Normalized growth rate versus $\frac{e}{(3\pi\nu d_H)} c_b E_0$ (see equation 4.1) for positive (c) and negative (d) nanocrystals. (e) Initial current density versus applied field E_0 . (f) Initial current density plotted against $\frac{e^2}{(3\pi\nu d_H)} c_b E_0$ (see equation 4.2). (g) Initial current density plotted against $\frac{e}{A} (|\dot{N}_0^{anode}| + |\dot{N}_0^{cathode}|)$. (h) Initial growth rate plotted versus $(1.5 \times 10^{-21} \frac{m^4}{s N/C}) \frac{c_b}{d_H} E_0$. Solid black line is the linear least square fit to the data. The dashed blue lines represent the 80 % prediction band.

The faradaic current measures the number of electrons that transfer across the interface. Figure 4.4e displays the initial current density, j_0 , as a function of applied electric field for all sample sets. The individual data-sets are linear but are dispersed across ~ 2 decades of current density-range. As Equation 2.13 illustrates, the current density is related to the carrier density, the charge, the mobility and the electric field for single types of positive and negative charge carriers as follows:

$$j_0 = \frac{e^2}{3\pi\nu d_H} (f_p z_p^2 + f_q z_q^2) c_b E_0, \quad (4.2)$$

Figure 4.4f shows that the current density profiles collapse to a line when the normalized current density is plotted against $\frac{e^2}{3\pi\nu d_H} c_b E_0$. The slope of this plot ($f_p z_p^2 + f_q z_q^2$) is 0.44 ± 0.07 , where the uncertainty is largely due to the particle size-dispersion.

By comparing the particle growth rate, $\dot{N}$, with the current density, these measurements quantitatively correlate the number of nanocrystals and the number of electrons. We show this correlation by plotting the initial current density (j_0) versus $\frac{e}{A} [|\dot{N}_0^{anode}| + |\dot{N}_0^{cathode}|]$. Figure 4.4g shows that the data essentially collapse to a line with a slope of 1.1 ± 0.02 . This fit is of good quality ($R^2 = 0.97$). The near-unity slope implies that $j_0 \cong \frac{e}{A} [|\dot{N}_0^{anode}| + |\dot{N}_0^{cathode}|]$. Formally, its slope (using equations 4.1 and 4.2) is given by Equation 2.15, which we re-write here:

$$m = \frac{f_p z_p^2 + f_q z_q^2}{s_p(0) f_p z_p + s_q(0) f_q |z_q|} \sim 1 \quad (4.3)$$

Although we have six independent variables, the values are constrained with sticking coefficients, $0 \leq s_p(0) \leq 1$, $0 \leq s_q(0) \leq 1$, the fraction-charged, $f_p + f_q \leq 1$. Therefore, the quadratic charge dependence in the numerator and linear charge dependence in the denominator enforces the requirement that the slope can only be 1 when $s_p(0)$, $s_q(0)$, z_p , and $|z_q|$ are 1. For integer nanocrystal charge we conclude that $s_p(0)$, $s_q(0)$, z_p , and $|z_q|$ must all equal unity. With s and z set to one, the initial fraction of positive and negative charge in

the suspensions can be determined from the slopes that we determined above for Figures 4.4c and 4.4d. That is, as Equation 4.1 indicates, we equate the slope of 0.18 for Figure 4.4c to $s_p(0)f_p z_p$. Knowing that $s_p = z_p = 1$ yields $f_p = 0.18 \pm 0.03$. Likewise, we determine $f_q = 0.20 \pm 0.03$. These values are in good agreement with Figure 4.4f as the slope of this plot, given by Equation 4.2, requires that $f_p + f_q = 0.44 \pm 0.07$. Our determinations of f_p and f_q are consistent with this requirement, within experimental uncertainty. Finally, as we have shown in section 2.2.2, the observation that the slope given by Equation (4.3) is essentially equal to unity indicates that (predominantly) only single types of positive and negative charges are present in the solutions.

Knowledge of s , f , and z at early time allows their substitution back into Equation 4.1 to fully quantify the proportionality between the early time growth-rate and the applied field. Recognizing that f_+ and f_- are equal within experimental uncertainty, we set $f_+ = f_- = 0.19$ in Eqn. (1), obtaining

$$\dot{N}_0 = (1.5 \times 10^{-21} \frac{m^4}{s N/C}) \frac{c_b}{d_H} E_0. \quad (4.4)$$

The factor in parentheses is the quantity $(s(0)fzeA)/3\pi\nu$, which we have evaluated using the quantities reported above, a viscosity of $\nu = 2.8 \times 10^{-4} P$ for the hexane, and an electrode-area of $A = 1.28 \times 10^{-4} m^2$. Equation 4.4 indicates that particle concentration c_b and size d_H are the main properties that control the response of the growth-rate to the applied E-field. In the present study, controlling c_b and d_H varied this response-function by an order of magnitude (from $2.0 \times 10^{11} ((particles)/(sm^2N/C))$ to $3.5 \times 10^{12} (particles/(sm^2N/C))$), demonstrating the ability to optimize the system for, say, maximal growth rate with a limited E-field range. We have predicted the growth rate for all 178 of our early time samples by substituting the corresponding c_b , d_H , and E_0 values into Equation 4.1. The observed growth rates are plotted against the predicted values in Figure (4h). The line is the linear least-squares fit, which has a y-intercept of 0.00 and a slope of 1.00, demonstrating that Equation 4.4 quantitatively predicts the growth rate. The scatter is due to uncertainties in the measured growth rates and the quantities in Equation 4.4; 80 % of the data lie within

$\pm 0.2 \times 10^{11}$ (particles/s) of the best-fit line as indicated by dashed blue lines. These findings, to our best knowledge, constitute the first demonstration of nanoparticle films grown by EPD where linearity between growth rate and applied field was both observed and fully quantified.

We estimate the fraction of nanocrystals expected to become thermally charged by considering the Born Gibb's energy of solvation, $\nabla G_{sol} = \frac{(z^2 e^2)}{(4\pi\epsilon_0 d)}(1 - 1/\kappa)$ [137; 138]. For particles with core diameters, d , in the range of 9.9-16.1 nm, and the fraction of neutral particles is $\sim 75\%$, the fraction of singly charged particles is $\sim 25\%$ (half being positive and the other half negative), the fraction of particles that are more highly charged is negligible. The observed charge distribution qualitatively agrees with the thermal charge distribution: a predominance of neutral and singly charged particles with equal positive and negative fractions and negligible fractions of more highly charged particles.

4.4.2 Steady state period

As can be observed from Figure 4.2a, the current and mass trajectories have similar exponentially dependent temporal evolution with similar time constants; this leads to approximately time-independent behavior after ~ 50 s. In the analysis above we considered the early time behavior less than 1s, during which the electric field and nanocrystal concentrations can be considered spatially homogeneous between the electrodes (Figure 4.3a). We now consider the long-time behavior after the nanocrystals have redistributed in response to the electric field and both the mass and the current have reached a new steady-state (Figure 4.3b). Our measurements in this time regime establish (as expected) that the nanocrystals redistribute to screen the electric field and allow us to estimate the interfacial field and interfacial field gradients. These, in turn, provide an estimate of the induced dipole moments of the nanocrystals and the dielectrophoretic forces near the electrode interfaces.

In the steady-state time-regime, the cell can be approximated as being composed of three regions, an interfacial region at the anode, an interfacial region at the cathode, and a bulk-like region between them as depicted schematically in Figure 4.3b. The interfacial regions are composed of the deposited nanocrystal films and a screening layer composed of charged

nanocrystals that extends over an effective Debye length. In this region near the electrode interface, we expect the electric field to be a function of the distance from the electrode, x , and in particular, to decay exponentially with x when charges are present. However, in the bulk-like region, between the two interfacial regions, the charged particle concentrations are approximately uniform, and the voltage drop across the bulk, V_b , changes linearly from the anodic side to the cathodic side, resulting in an essentially constant electric field, E_b .

If the densities of charged particles do not change in the three regions, then the current density must be the same in the three regions and given by $j = \sigma(x)E(x)$, where σ is the conductivity. The normalized current density $j(t)/j_0$ from 45 different samples (Figure 4.2c) essentially overlap and decay exponentially from an initial value of unity to a steady level of ~ 0.8 on a ~ 14 s time-scale. Thus, in the steady-state regime, 3 time constants beyond the transient decay, the steady-state current density is $j_{ss} = j(t) > 42s \sim Bj_0$ where $B = 0.7$. At the interfaces, the conductivity and electric fields can be complicated functions of position, x ; however, in the bulk region the conductivity and the electric field are approximately constant,

$$j_{ss} = Bj_0 = \sigma_b E_b = \sigma_b V_b / L_b \sim \sigma_b V_b / L \quad (4.5)$$

where subscript b indicates the bulk region and L is the distance between the electrodes. Here we assume that the concentration of charged nanocrystals in the bulk does not change due to film growth (rationale given in Appendix A) and that the interface thickness is much smaller than the electrode spacing so that $L_b \sim L$. At time zero we know that $j_0 = \sigma_b E_0 = (\sigma_b V)/L$. Substituting j_0 into Eq. 4.4, implies that the voltage drop across the bulk region is $V_b = BV$ where V is the applied potential.

After establishing the voltage drop in the bulk, we can estimate the voltage drop across the two interfacial regions. As stated above, $B = 0.7$ for our system. This finding implies that 30 % of the applied voltage decays across the two interfacial regions, which are microscopic (< 200 nm) in extent. Such rapidly decaying voltage profiles are indicative of electrolytic screening at the interfaces. We attribute the screening to charges that are dispersed in the

film (in analogy to Thomas-Fermi screening [139; 140]) and in the adjacent solution (Debye screening). As will be shown, our steady-state results are more consistent with much of the charge being dispersed in the film, as shown schematically in Figure 4.3b. Thapa, *et. al.* have worked out a theoretical description for the electric potential in an electrolytic cell when both screening and steady-state current-flow occur [72]. We use this theory to describe the potential in the cell:

$$V(x) = \frac{V}{2}(-K_1 e^{x/\lambda_{int}} - K_2 e^{-x/\lambda_{int}}) - \frac{VB}{L}x + K_3, \quad (4.6)$$

where λ_{int} is an effective screening length associated with interfacial region (film + adjacent solution). The coefficients K_1 , K_2 , and K_3 depend on λ_{int} , the cell length L , the quantity B (defined above), and the balance between cathodic and anodic voltage drops, which we call β . These coefficients are reported in Chapter 2. Invoking the general relationship $E(x) = -\frac{dV(x)}{dx}$, we obtain the interfacial field profile in the cell from which we derive estimates of the field strength at the surface of anodic and cathodic films:

$$E(\delta_{an}) \cong \frac{-V}{2\lambda_{int}} K_2 e^{-\delta_{an}/\lambda_{int}} \quad (4.7a)$$

$$E(\delta_{ca}) \cong \frac{V}{2\lambda_{int}} (e^{\frac{L}{\lambda_{int}}} K_1) e^{-\delta_{ca}/\lambda_{int}}. \quad (4.7b)$$

The derivation of these equations is given in Chapter 2. Below we will use Equation 4.7a and 4.7b to quantify the thicknesses of the anodic and cathodic films. To summarize, the asymptotic value of the current density gives a measure of screening at the interfaces. If the electrodes are perfectly screened ($B = 0$), the current density would go to zero and all of the voltage would drop across the interfacial regions. In the nickel nanocrystal case, the film and Debye layer only partially screen the field, allowing a current to flow.

To address the mechanism of film-growth, we note that the applied field is required to

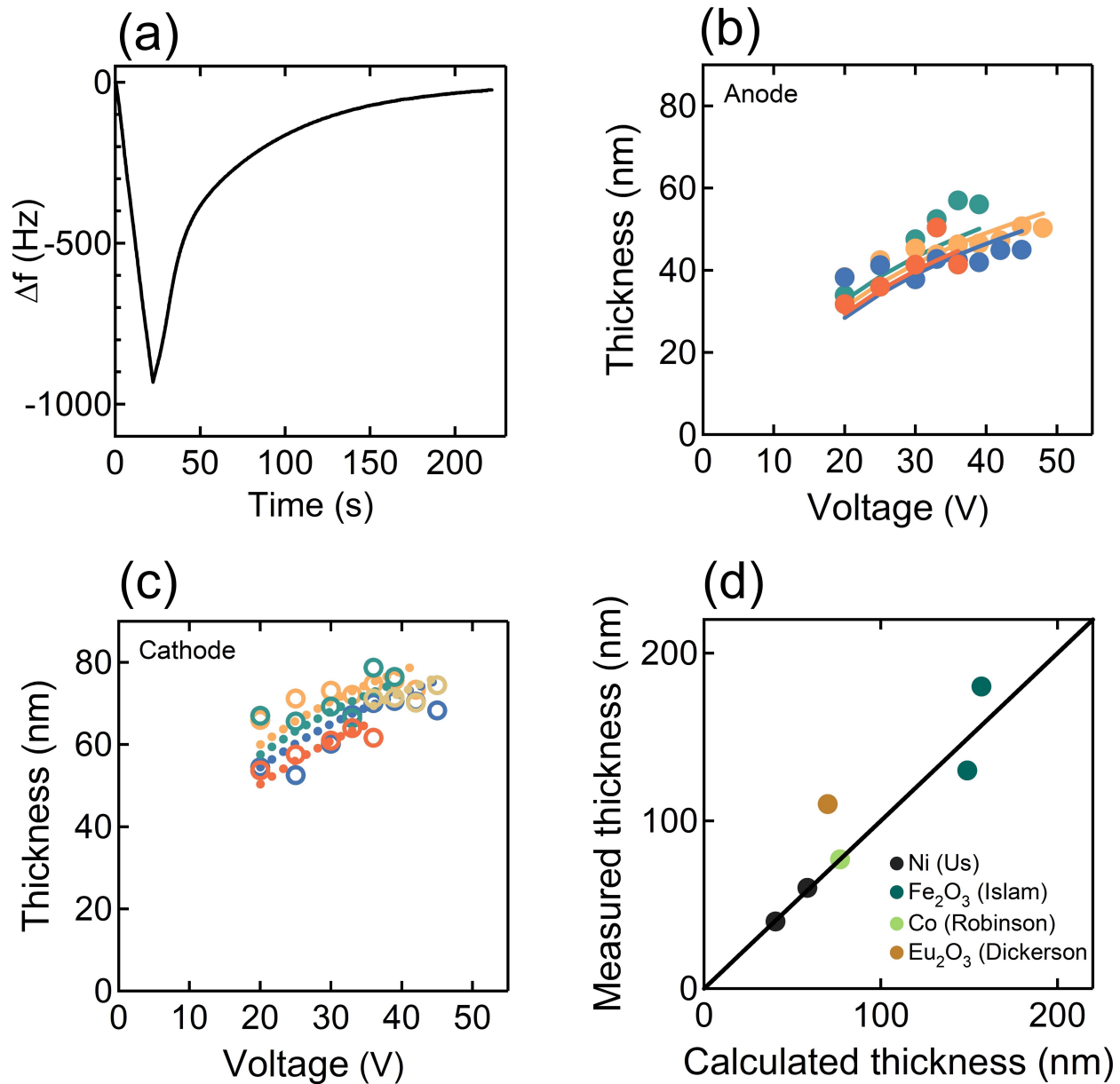


Figure 4.5: (a) The QCM frequency response showing film growth when the applied voltage is turned on for 20 s followed by the film dissolution when the voltage is turned off. (b) and (c) are the film thickness plotted against applied voltage V at anode and cathode, respectively. The solid and dashed lines are the fits using Equation 4.6. Different colors (red, green, blue, and yellow) in (b) and (c) represent different concentration ($4.59 \times 10^{20} \text{m}^{-3}$, $7.18 \times 10^{20} \text{m}^{-3}$, $8.55 \times 10^{20} \text{m}^{-3}$, $1.10 \times 10^{21} \text{m}^{-3}$). (d) Measured thickness from different literatures including ours (black filled circles) plotted versus calculated thickness using Equation 4.6. The solid line passes through the origin and has slope of unity.

initiate growth and that the film rapidly dissolves when the field is turned off. Figure 4.5a plots the frequency response showing film growth for 20 s when the field is present. The plot

also shows that the film dissolves after turning off the field. The dissolution behavior indicates that the nanocrystals are reversibly bound to the interface and to each other. Furthermore, at long times (~ 42 s), film-growth essentially stops although the current continues to flow. Together, these observations suggest that the electric field at the film surface weakens as the film thickens, eventually becoming too weak for further growth but still strong enough for charge-transfer to continue.

We next relate the final film thickness δ to the field at the film surface. A detailed derivation of this quantity is provided in Chapter 2. This analysis is based on the following findings. First, the current density is constant, so charge conservation dictates that the contributions from the positive particles j_p and negative particles j_q must equal. Second, the flux of positive particles out of the Gaussian pillbox at the interface (Figure 4.3b) can be written as $-\frac{1}{e} \times j_p$ (where j_p is the contribution of the current density due to the positive particles). And third, the flux of negative particles into the Gaussian pillbox in Figure 4.3b is $+\frac{1}{e} \times j_q$. Because $j_p = j_q$, the flux of *charged* particles into the pillbox sums to zero. For a film in steady state, the flux of depositing particles must balance the flux of dissolving particles. With no net flux from the charged particles, we now consider the neutral particles.

We visualize the interfacial regions as depicted in Figure 4.3b, where the neutral particle concentration, the concentration-gradient, the E-field, and the E-field gradient are large relative to their values in the bulk. In turn, we hypothesize that *diffusion* and *dielectrophoresis*, whose magnitudes scale directly with these quantities, will be the most important processes affecting the neutral particles in the interfacial region. In this physical picture, mass conservation at an interface is expressed as the following continuity equation: $J_{D,n} + J_{DEP,n} = 0$. The diffusive flux has the form $J_{D,n} = -D\nabla n(x)$, and the dielectrophoretic flux $J_{DEP,n} = \frac{\alpha E(x) \cdot \nabla E(x)}{\zeta} n(x)$, where $n(x)$ is the concentration of neutral particles at position x , α is the nanocrystal polarizability, and ζ is the coefficient of viscous friction which can be expressed as $\zeta = 3\pi\eta d_H$ for spherical particles in a solvent with viscosity η . Solving the continuity equation for neutral particle concentration at the surface of the anodic film where $x = \delta_{an}$, we find $n(\delta_{an}) \cong n_b e^{\frac{\alpha E^2(\delta_{an})}{2k_B T}}$, where n_b is the bulk neutral particle concentration. (Details in Chapter 2). Using Eqn. 4.7a, we substitute for $E(\delta_{an})$ to

obtain $n(\delta_{an}) \cong n_b e^{\frac{\alpha K_2^2 V^2}{8k_B T \lambda_{int}^2} e^{-2\delta_{an}/\lambda_{int}}}$. Rearrangement of this equation yields the anodic film thickness δ_{an} :

$$\delta_{an} \cong \frac{\lambda_{int}}{2} \ln \left[\frac{\alpha K_2^2 V^2}{8k_B T \lambda_{int}} - \ln \ln \frac{n(\delta_{an})}{n_b} \right] \quad (4.8a)$$

An analogous set of steps provides an equation for the cathodic film thickness δ_{ca} :

$$\delta_{ca} \cong \frac{\lambda_{int}}{2} \ln \left[\frac{\alpha (e^{L/\lambda_{int}} K_1)^2 V^2}{8k_B T \lambda_{int}} - \ln \ln \frac{n(\delta_{ca})}{n_b} \right] \quad (4.8b)$$

Thus, we have arrived at theoretical expressions for the terminal thicknesses of the anodic and cathodic films in terms of three unknown fitting parameters: the screening length, λ_{int} , the concentration of neutral nanocrystals at the film-solution interface, $n\delta$, and the balance between cathodic and anodic drops, β (which K_1 and K_2 depend upon).

Figure 4.5b and 4.5c plot the measured film thicknesses versus the applied voltage V for the anodic and cathodic electrodes, respectively. Each sample consisted of 16.5 nm diameter nanocrystals and, therefore, had the same polarizability (which depends on nanocrystal volume). The different colors represent different nanocrystal concentrations. The lines are best-fits of Equations 4.8a and 4.8b for each concentration data-set. We attained these fits by permitting three fitting parameters. First, we have used a common value of λ_{int} , 26 nm, and $n(\delta)$, $2.05 \times 10^{21} \text{ m}^{-3}$, for both anodic and cathodic data-sets. λ_{int} arises naturally in the theory, describing the effective, interfacial screening length, and is common to both anodic and cathodic interfaces. We interpret $n(\delta)$ —the neutral particle concentration at the film-solution interface—as the solubility of 16.5 nm particles in hexane. The film is stable when the local concentration is equal to the solubility, but is undersaturated and dissolves when the concentration is smaller. A common fit parameter for all data sets is justified as we expect the solubility to be the same for both the anodic and cathodic films. The third fitting

parameter β is the balance between the cathodic and anodic voltage drops. We observe some asymmetry in the film-thickness, suggesting differing capacitances of anodic and cathodic interfaces and, in turn, different interfacial voltage drops. The need for this fitting parameter supports this picture. We have employed β -values between 1.1 and 1.2 to fit the data-sets in Figures 4.5b and 4.5c. Slower charge transfer kinetics within the cathodic film is a possible cause of the larger voltage drop.

To further test the validity of our thickness-prediction, we have used Equations 4.8a and 4.8b to predict the values for film thicknesses reported in the literature [55; 58; 66; 71; 127]. These systems are similar to our Ni nanoparticle system in that all report either time-dependent current density or mass profiles indicating that the films reach a steady-state. Additionally, like the present study, all used hexane as the solvent and oleic acid as the ligand. In all of these systems, the dielectric constant of the nanoparticles is greater than that of solvent, as required for the nanoparticles to dielectrophorese towards field-maxima. Figure 4.5d plots the measured steady-state thicknesses (our values are the black filled circles) versus the predicted thicknesses that we found using Equations 4.8a and 4.8b. To calculate the film-thicknesses, we have used our determinations for λ_{int} . The fraction B was calculated using the reported current density profile. For the systems where the current density is not reported, we applied our value for B . We have used the reported particle sizes to calculate the polarizability of nanocrystals for these systems. For the case where only core size is reported (Eu₂O₃ system), we have added a 2 nm ligand contribution to the size. These quantities are tabulated in Appendix A.

To a significant degree, the data in Figure 4.5d fall on a line of unity slope (solid black line). This observation demonstrates that for systems similar to ours, Equations 4.8a and 4.8b are reasonably successful at predicting the terminal film thickness. In turn, this finding suggests that the interfacial field plays a significant role in holding the neutral nanocrystals near the electrode interface via dielectrophoretic forces. This mechanism is expected to be important in cases where the interaction potential between the neutral nanocrystals is small and reversible. In such cases, dielectrophoretic trapping is a possible mechanism for maintaining a sufficient concentration to exceed the film solubility limit.

4.5 Conclusions

In summary, we provide a comprehensive analysis of electric-field assisted nanocrystal film formation using oleic acid coated nickel nanocrystals dispersed in hexane as a case study. Our analysis shows that electric-field assisted growth is a complex process where migration, diffusion, and dielectrophoresis play significant roles. To untangle these effects, we have coupled current-measurements with mass-measurements using a purpose-built double QCM. By correlating the mass and charge transfer kinetics, we have determined the nanocrystal charges, the concentrations of the positively and negatively charged nanocrystals, and their initial sticking coefficients. We verify that the charge distributions found from correlating mass and current are in reasonable agreement with the Born-Gibbs approximation for thermally charged nanocrystals, which is commonly assumed in the EPD literature. We further show that the system reaches a steady-state where the interfacial field strength and the magnitudes of the diffusive and dielectrophoretic fluxes of neutral particles determine the terminal film-thicknesses. This relationship also gives a means to estimate nanocrystal solubility which is otherwise difficult to measure. From the steady-state analysis we derive a relationship between the film thickness and process parameters such as voltage and nanocrystal concentration. We have tested the predicted film thicknesses against a broad range of process conditions as well as several other metals and metal-oxides systems found in the literature. Overall, this study demonstrates that a quantitative approach to electric field-assisted deposition of nanocrystal films can quantify important nanocrystal properties that are generally difficult to measure. These include fundamental properties such as the nanocrystal charge, the fraction of charged nanocrystals, and the nanocrystal solubility; as well as practical properties such as the relationship between film thickness and process conditions.

4.6 Acknowledgements:

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Chapter 5

Conclusions and future directions

5.1 Conclusions

We have presented a systematic study of metallic nanoparticle thin film-formation using electric field-assisted assembly. The ligated nickel nanocrystals used in this study had oleic acid ligands and were dispersed in hexane prior to deposition. The deposition was carried out in extremely mass-sensitive Quartz Crystal Microbalance (QCM) electrodes. We coupled two QCMs together using a custom-designed locking-ring assembly. This arrangement allowed us to measure mass at both electrodes simultaneously. The core diameter of the nanocrystal ranged from 9.9 nm to 16.1 nm with a polydispersity of $\sim 10\%$. We varied the nanocrystal concentration from $4.22 \times 10^{20} \text{ m}^{-3}$ to $4.02 \times 10^{21} \text{ m}^{-3}$.

This work has demonstrated that in the nickel nanocrystal assembly, the nanoparticles are the only charge carrier (negligible current and no mass growth at both electrodes during control experiments) in the suspension. The applied electric field drives the charged nanocrystal in the suspension towards the respective electrode surfaces where they become neutral via charge transfer with the electrode. This fact was supported by the observed films at both anode and cathode. We observed that the early-time film growth rate at both anode and cathode scales linearly with the applied field as predicted by the theory ($\frac{\dot{N}_0^{an}}{A} = (s_q(0)f_q c_b \mu_q)E_0$). This finding shows that nanocrystal concentration (c_b) and parti-

cle size (d_H) are the main properties that control the linear response of the growth rate to an E-field of a given strength. By controlling these properties, we have demonstrated variation of this proportionality factor across an order of magnitude (from $2.0 \times 10^{11} \text{ C/Nsm}^2$ to $3.5 \times 10^{12} \text{ C/Nsm}^2$). These findings, to our best knowledge, constitute the first demonstration where linearity between growth rate and applied field was both observed and fully quantified.

In this work, we have coupled the double-QCM method to electrophoretic deposition. This allowed us to monitor the growth rate at both electrodes *in situ* simultaneously with the current. This novel method provided a way to correlate the mass and charge transfer kinetics at early-time and hence to realize quantitative EPD. The correlation resulted in the important growth parameters of the nanocrystal assembly: charge on the nanocrystal ($z = 1$), the fraction of charged nanocrystals ($f = 38\%$, both positive and negative species combined), and initial sticking coefficient ($s(0) = 1$). This study also suggested that (predominantly) single charged species of positive and negative nanocrystals are present in the suspension. Furthermore, using the steady-state values for mass and current, we estimated the interfacial field that we used to predict film thickness in terms of process parameters such as concentration and voltage. That analysis also resulted in the neutral nanocrystal concentration at the film-solution interface which we interpreted as nanocrystal solubility. In addition to that, our findings from the analysis of terminal film thickness were applied to predict, to a reasonable degree, the film thickness reported in the literature. The success of this analysis supported the fact that the interfacial field plays a key role in holding neutral nanocrystals near the electrode surface dielectrophoretically— a possible mechanism of film growth.

5.2 Future Directions

Modern electronic devices are heading toward nanocrystal-based structures due to their size-tunable properties and low integration cost into devices. While the structures of nanocrystals have been extensively investigated, little research has been done in situ for the full assembly process. To improve the situation, detailed quantitative information on nanocrystal assembly is needed where the crystallization process can be precisely controlled. In this venue, this work is an advancement.

Quantitative EPD is essential to fill the knowledge gap which lacks accurate prediction of the film properties: growth rate, and film thickness. A major challenge to this is that the suspension composed of nanocrystals that might have particles of multiple sizes. Systems with polydispersity in particle size may still have growth rates linear with the field but the response that results will have a complicated dependency on the solution properties. In such a scenario, it is much more difficult to de-couple the contribution of each size to the growth rate. Moreover, the size uniformity of nanocrystals is an important parameter in nanotechnology. The majority of wet synthetic approaches that are employed to synthesize nanocrystals yield polydispersed nanocrystals. To realize nanocrystal structures with well-defined properties, which modern technology demands, it is necessary to reduce the polydispersity in size. For example, surface plasmon resonance [141] and magnetic properties [142] are highly dependent on particle size. So, nanocrystal structures composed of polydispersed particles will severely complicate the overall properties of the entire structure. Furthermore, in biomedical applications, nanocrystal coated with antibodies can regulate cell functions. The study performed with gold and silver nanocrystal demonstrated that nanocrystal having sizes 40 *nm* and 50 *nm* showed the greatest effect [143]. The narrow size distribution of particles is thus desirable to synthesize nanocrystal structures with precise functional properties.

To deal with the polydispersity in size, we can use the electric field to separate particles of different sizes. If the particle in the suspension acquires charge by absorbing ions from the medium, then its probability of charging is directly proportional to the surface area of

the particle, $Q \propto d^2$. Where Q is the charge on the particle and d is its diameter. Under the application of an external electric field, the charged particles move to the electrode of opposite polarity and experience the drag force from the solvent. In equilibrium, the drag force is balanced by electrostatic force by the field.

$$QE = 3\pi\nu dv. \quad (5.1)$$

Where E is applied electric field, ν is the viscosity of solvent, and v is drift velocity. With rearrangement, Equation 5.1 yields:

$$v = \frac{QE}{3\pi\nu d}. \quad (5.2)$$

Since

$$Q \propto d^2, v \propto d.$$

Hence, the larger particles drift faster than the smaller particles in the given solvent under the influence of the same external field. In addition, the diffusion coefficient of the particles, D , is given by the expression $D = kT/3\pi\nu d$, where k is the Boltzmann constant and T is the temperature. Hence, the larger particle diffuses slowly as compared to the smaller particles. Therefore, once the electric field is applied, the larger particle gets to the electrode surface first where it stays there for longer periods of time as compared to the smaller particle because of having a smaller diffusion coefficient. This size-selective behavior of particles aggregates the larger particles near the electrode surface and smaller particles towards the bulk thereby creating a distinct band of particles of different sizes.

Nanocrystals composed of magnetic materials such as iron oxide nanocrystals can be separated using the magnetic field. The magnetic force acting on the magnetic nanocrystal is given by $\mu_0\chi V_p H \nabla H$ [144]. Where μ_0 is the permeability of free space, χ is the difference between the volume magnetic susceptibility of the particle and surrounding medium, V_p is the particle volume, and H is the applied magnetic field. This force depends strongly on

the particle size and gradient of the magnetic field, ∇H . In a uniform magnetic field, the force experienced by the nanocrystal will be zero. This magnetic method is found very effective to separate the particle with narrow size distribution. It has been observed that Fe_2O_4 nanocrystals whose size ranges from 4 nm to 12 nm were separated by using a gradient magnetic field [145].

Another method could be the use of the difference in density between the suspended particles and the solvent. If the particles are denser than the solvent, they sediment under gravity. However, for the small nanocrystals, only gravitational energy will not be enough as is counterbalanced by the thermal energy. In such a situation, centrifugation helps. The centrifugation is based on three main forces acting on the suspended particles. The centrifugal force, $(\rho_p V_p \omega^2 R)$, acts away from the axis of rotation. Where ρ_p is the density of suspended particles, V_p is the volume of particles, R is the particle distance from the axis of rotation, and ω is the angular velocity. The other forces acting on the particles are buoyant force $(\rho_s V_p \omega^2 R)$ and frictional force (γv) . Where ρ_s is the density of solvent, γ is the frictional coefficient, and v is the particle velocity. At equilibrium, the centrifugal force is balanced by the sum of buoyant force and frictional force due to solvent. Hence, at equilibrium the particle moves with the constant velocity given by $v = \frac{V_p(\rho_p - \rho_s)\omega^2 R}{\gamma}$. This velocity depends on the size of the particles, the density difference between the particle and solvent, the rotational speed of the rotor, and the size of the centrifuge. Hence, centrifugation helps to differentiate particles into distinct bands according to their size as $V_p \propto d^3$.

Size exclusion chromatography (SEC) is another powerful tool to separate the particle according to their hydrodynamic size. This technique is based on the principle that the small particles are trapped in the pores of the stationary phase and elute last while larger particles move freely with the eluent and exit the column first. Using conventional silica columns as a stationary phase with pore size 50-100 nm and aqueous trisodium citrate as eluent, gold nanocrystals (2.9 nm to 20 nm) were separated [146]. In another study, inorganic colloids with sizes ranging from 1-50 nm were separated [147]. For this study columns of porous silica microspheres of size $< 10\mu\text{m}$ were used. Furthermore, a study on CdS using sephacryl gel demonstrated a linear relationship between the logarithm of the particle size and the elution

time [148]. To apply this method in an effective way, proper eluent and stationary phases should be considered.

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Appendix A

Supporting Information

A.1 Correlation of Measured Quantity (Frequency Shift) to Mass, Number of Nanocrystals, and Film Thickness

To generate the table [A.1](#) from the measured frequency shift (Δf), we have used the following conversion relations:

$$m = (6.99 \times 10^{-9} (g/Hz)) \Delta f, \quad (\text{A.1a})$$

$$N = \frac{m}{\rho_{np} V_{np}}, \quad (\text{A.1b})$$

$$\delta = \frac{3N}{4A} d_H^3, \quad (\text{A.1c})$$

where m is the deposited mass, N is the number of nanocrystals, ρ_{np} is the density of nanocrystal, V_{np} is the volume of nanocrystal, δ is the film thickness, A is the area of

electrode, and d_H is the hydrodynamic size of nanocrystal.

Table A.1: *Correlating frequency, mass, number of nanocrystals, and film thickness.*

field (V/m)	Frequency shift (Hz)	Mass ($\times 10^{-6}g$)	# of NC ($\times 10^{12}$)	thickness (nm)	thickness (ML)
982.8	730	5.10	1.58	39	2.7
1228.5	809	5.66	1.76	43	3.0
1474.2	863	6.04	1.87	46	3.2
1621.6	835	5.84	1.81	45	3.1
1769.0	882	6.17	1.91	47	3.3
1916.5	886	6.19	1.92	47	3.3
2063.9	901	6.30	1.96	48	3.4
2211.3	966	6.76	2.09	52	3.6
2358.7	958	6.69	2.08	51	3.6

A.2 Calculation of Nanocrystal Concentration

We calculated bulk concentration in m^{-3} from mg/ml employing the conversion relation:

$$m^{-3} = \frac{mg/ml \times 1000}{\rho_{np} V_{np}} \quad (A.2)$$

The values are summarized in table [A.2](#).

Table A.2: *Nickel nanocrystal concentration and diameter*

Sample	Symbol color used in plots	d_H (nm)	c_b (mg/ml)	c_b (particles m^{-3})
1	●	13.9	17.0	3.19×10^{21}
2	●	15.0	15.0	2.09×10^{21}
3	●	15.0	30.0	4.19×10^{21}
4	●	16.5	2.7	2.65×10^{20}
5	●	16.5	4.5	4.41×10^{20}
6	●	16.5	5.4	5.29×10^{20}
7	●	16.5	7.1	6.90×10^{20}
8	●	16.5	8.5	8.22×10^{20}
9	●	16.5	11.0	1.06×10^{21}
10	●	17.0	14.0	1.22×10^{21}
11	●	17.5	2.6	1.99×10^{20}
12	●	17.5	5.1	3.98×10^{20}
13	●	17.5	6.7	5.24×10^{20}
14	●	17.5	10.3	8.02×10^{20}
15	●	20.1	9.0	4.22×10^{20}

A.3 Control Experiments

To determine background sources of either mass or charge, we ran control experiments in pure hexane (Figure A.1a) and hexane with 1mM oleic acid (Figure A.1b). In both controls, the current density and the frequency shift are negligible indicating that neither hexane nor oleic acid within the solvent contributes to mass or charge transfer in our experiments.

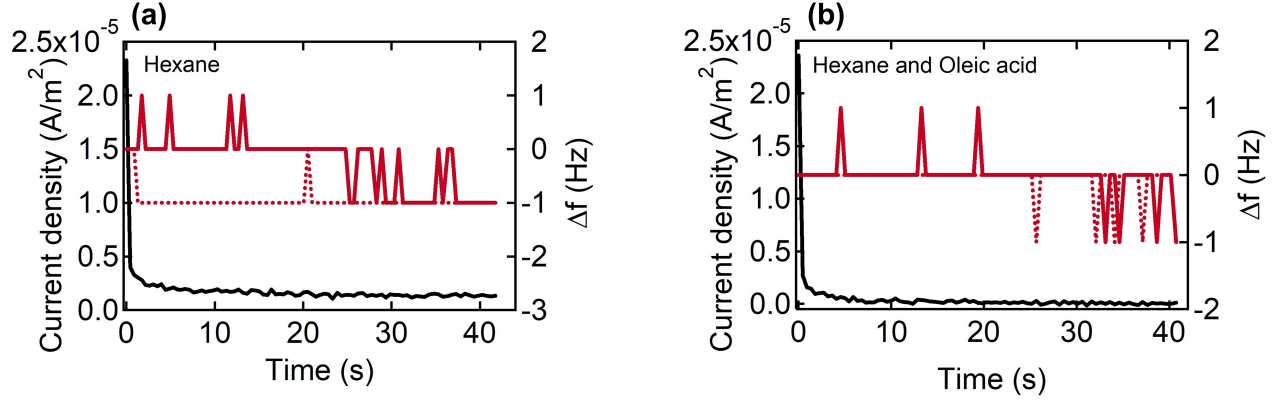


Figure A.1: Control experiments in Hexane (a) and in Hexane and Oleic acid mixture (b). In both panels, the solid black line is the current density profile during the V-step of 20 V measurement. Red solid and dashed lines are the frequency shifts measured at anode and cathode respectively.

A.4 Change in Bulk Concentration due to Deposition

Table A.3: Showing insignificant change in bulk concentration due to film growth.

Batch	Voltage (V)	Volume of cell (ml)	Bulk concentration (m^{-3})	Number of deposited NC on both electrodes	% change in bulk concentration
1	20	9.0	3.19×10^{21}	2.72×10^{12}	0.01
2	20	9.0	2.09×10^{21}	1.57×10^{12}	0.01
3	20	6.0	4.19×10^{21}	5.35×10^{12}	0.02
4	20	6.0	1.06×10^{21}	4.54×10^{12}	0.07
5	20	9.0	1.22×10^{21}	1.22×10^{12}	0.01
6	30	6.0	8.02×10^{20}	4.21×10^{12}	0.08
7	20	9.0	4.22×10^{20}	4.09×10^{12}	0.01

A.5 Process Parameters and Film Thickness

Table A.4: *Process parameters and film thickness.*

Applied field (V/m)	Bulk concentration (m^{-3})	Film thickness at anode (nm)	Film thickness at cathode (nm)
333-533	3.19×10^{21}	15-21	11-15
266-666	2.09×10^{21}	10-16	8-14
295-885	4.09×10^{21}	31-49	14-30
983-2360	2.65×10^{20} - 1.06×10^{21}	32-52	—
167-600	1.22×10^{21}	8-15	8-19
200-666	4.22×10^{20}	5-11	3-11

A.6 GISAXS to Measure Film Structure

An incident angle of 0.21 degrees was used for GISAXS measurements. To determine lattice constants, we used the in-plane q_y values collapsed onto the Yoneda line as these do not have shifts modified by refraction. Horizontal linecuts were extracted from the 2D data at the Silicon Yoneda line at $q_z = 0.0441/\text{\AA}$. An exponential background was fit to the linescans using regions without peaks - near the origin and at large q_y values. Peak fitting of the background-subtracted linescans were used to extract the peak position using a Lorentz lineshape.

A.7 Ex situ Characterization of Nanocrystal Films Deposited Using EPD

Nickel nanocrystal films deposited directly on to the quartz substrates were difficult to characterize ex situ because they could not be removed from the QCM holder without disrupting the film. In addition, the gold film introduced roughness making it unsuitable for GISAXS. For this reason, we used gold-backed, doped silicon substrates to make films for ex situ

characterization. Our setup, which employed a parallel plate geometry [149], allowed us to remove the electrodes from solution while maintaining a voltage so that the films did not dissolve back into solution during removal.

Scanning electron microscopy (SEM) and GISAXS were used to characterize Ni nanocrystal films deposited on the positive and negative electrodes using a 300 V/m field. At large scale, SEM images (Figures A.2a and A.2b) shows conformal films on both electrodes. Images at higher magnification (Figures A.2c and A.2d), show that film is composed of two layers of nanocrystals and has hexagonal symmetry parallel to the substrate.

GISAXS measurements confirm thin films as noted by streaks in the vertical direction (Figure A.2e and A.2f). The spot positions are consistent with a distorted FCC lattice oriented with the 111-facet parallel to the substrate. The in-plane lattice constant is larger than the out-of-plane lattice constant, which has been attributed to a contraction in the vertical direction film during drying.

The lattice constant obtained by fitting the horizontal peak positions was $a = 27.1 \text{ nm}$ which implies a center to center distance of 19.2 nm . From solution SAXS, the nanocrystal core diameter for this batch of nanocrystals measured 15 nm (or $\sim 19 \text{ nm}$ with extended oleic acid ligands). The similarity between the lattice constant and the nanocrystal diameter suggests that the oleic acid is not interdigitating in these films.

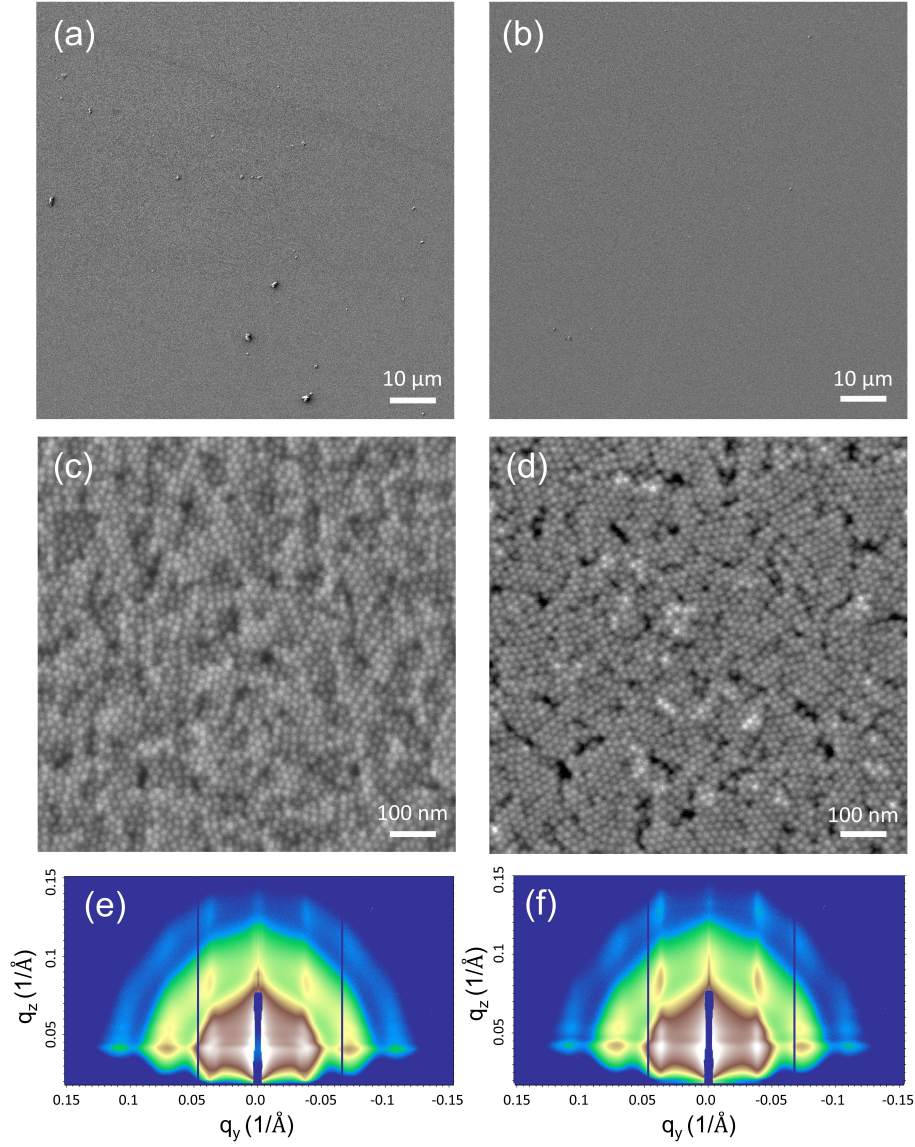


Figure A.2: SEM images of Nickel nanocrystals film prepared via electrophoretic deposition at anode (a) and cathode (b). The scale bar is 10 μm. The high resolution image of the film at anode (c) and cathode (d). The scale bar is 100 nm. GISAXS pattern of Nickel nanocrystal film at anode (e) and cathode (f).

A.8 Analysis for Film Thickness from Literature

Table A.5: *Parameters used to analyze film thickness from literatures.*

Nanocrystal type/ligand	Solvent	V (<i>volt</i>))	d_H (<i>nm</i>)	α (C^2mN^{-1})	c_b (m^{-3})	$\frac{n_n(\delta)}{n_{n,b}}$	B	β	Citation
Ni/OA	Hexane	30	16.5	2.7×10^{-35}	4.6×10^{20}	6.9	0.7	1.1	Us
Fe ₂ O ₃ /OA	Hexane	530	12.0	1.3×10^{-35}	4.0×10^{18}	2.7	0.14	1.0	[71]
Fe ₂ O ₃ /OA	Hexane	530	14.2	2.3×10^{-35}	5.2×10^{18}	3.2	0.14	1.0	[53]
Co/OA	Hexane	300	10.8	4.4×10^{-36}	1.8×10^{20}	1.7	0.7	1.2	[66]
Eu ₂ O ₃ /OA	Hexane	250	6.4 (*)	1.5×10^{-35}	2.0×10^{21}	1.5	0.8	1.0	[58]

* 2 *nm* ligand included

Appendix B

Controlled electrochemical growth of ultra-long gold nanoribbons

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Controlled electrochemical growth of ultra-long gold nanoribbons

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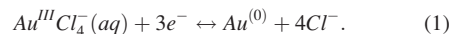
This paper describes the electrochemical growth of branchless gold nanoribbons with $\sim 40\text{ nm} \times \sim 300\text{ nm}$ cross sections and $>100\text{ }\mu\text{m}$ lengths (giving length-to-thickness aspect ratios of $>10^3$). These structures are useful for opto-electronic studies and as nanoscale electrodes. The 0.75–1.0 V voltage amplitude range is optimal for branchless ribbon growth. Reduced amplitudes induce no growth, possibly due to reversible redox chemistry of gold at reduced amplitudes, whereas elevated amplitudes, or excess electrical noise, induce significant side-branching. The inter-relatedness of voltage-amplitude, noise, and side-branching in electrochemical nanoribbon growth is demonstrated. Published by AIP Publishing. [<http://dx.doi.org/10.1063/1.4976027>]

Ultra-long nanowires and nanoribbons with aspect ratios $>10^3$ are useful samples for learning about fundamental opto-electronic processes, including ballistic and collective charge-transport on ultrafast time-scales.^{1–3} Such studies will benefit from monolithic wires long enough to allow the excitation to propagate between spatially separated pump- and probe-illumination sites. In the physiology-venue, branchless nanowires are promising neural⁴ and cellular probes.⁵ Directed electrochemical nanowire assembly (DENA)⁶ is a method for fabricating electrode-nanowire assemblies where the nanowire is a single crystal⁷ of tunable diameter⁸ and variable composition: In,⁷ Au,⁹ Cu,¹⁰ Pt,¹¹ and Pd.¹² Growth is caused by applying an alternating voltage across working and counter electrodes (CEs) that are immersed in a salt solution, stimulating the dendritic crystallization of the metallic species at the (sharper) working electrode (WE) during the negative half cycles.¹³ As the term *dendritic crystallization* suggests, the method tends to produce branched, TV-antenna-shaped structures, and one would like to control the degree to which side-branching occurs during the growth process. Prior applications of DENA have employed voltage-amplitudes of 4–8 V for Au,^{9,14} Cu,¹⁰ Pt, and Pd wires,^{11,12} and $\sim 16\text{ V}$ for In wires.⁷ These values are several times larger than the standard reduction potentials of the metals. Here we have employed electro-etched working electrodes having $<50\text{ nm}$ tip radii in order to realize growth at considerably lower amplitudes: 0.75–1.5 V. These factors enable the growth of *ultra-long* gold nanoribbons with length-to-thickness aspect ratios $>10^3$. A stability analysis illustrates how small voltages and minimal noise suppress the Mullins-Sekerka instability, rendering side-branching unlikely.

Figure 1(a) depicts the set-up for the DENA-based growth of gold nanoribbons.^{6,9} This apparatus is mounted on the stage of an inverted microscope (Leica, IRB) under ambient conditions and consists of an electrode pair immersed in aqueous KAuCl_4 solution. To confine the growth to its tip, the working electrode (WE) must be sharper than the counter electrode (CE). Hence, we fabricate the WE by electro-etching $200\text{ }\mu\text{m}$

diameter gold wire (Ted Pella) until its foremost radius is $<50\text{ nm}$.¹⁵ The scanning electron micrograph in Figure 1(b) and the inset show a typical WE with a $\sim 25\text{ nm}$ tip radius. The comparatively blunt CE (not shown), made from $500\text{ }\mu\text{m}$ diameter gold wire (Kurt J. Lesker), is electro-etched to a $\sim 2.5\text{ }\mu\text{m}$ radius. The CE is taped to a glass microscope slide that is mounted on the inverted microscope. The WE is mounted in a 3D stage and positioned to have $\sim 1\text{ }\mu\text{m}$ inter-electrode gap relative to the CE. A $\sim 20\text{ }\mu\text{l}$ aliquot of solution composed of aqueous 40.0 mM KAuCl_4 (Sigma) is deposited across the inter-electrode gap. Nanoribbon crystallization is induced by using a function generator (Hewlett Packard, 8116A) to apply a 10–50 MHz square-wave voltage signal to the WE, while grounding the CE. The profile in Figure 1(c) is a representative 37.0 MHz voltage signal. A small ($\sim +35\text{ mV}$) DC offset is also applied to prevent coating of the ribbon by polycrystalline gold. A component of this study requires the addition of a white-noise signal, supplied by a second function generator (Agilent, 33220A), to the square wave signal. A high bandwidth (4.0 GHz) summing amplifier is used to do so. The average growth velocity $\langle v \rangle$ of a nanoribbon is determined by collecting movies of its growth and computing the ratio $\Delta L/\Delta t$, where ΔL is the change in length and Δt the elapsed time. The surface of the microscope slide is made hydrophobic by coating it with poly-dimethyl silane (e.g., Rain-X), causing the solution drop to form a $\sim 90^\circ$ contact angle that permits the electrode-ribbon assembly to be pulled perpendicularly through the air-water interface—avoiding damaging lateral forces during extraction.

The cyclic voltammogram (CV) in Figure 1(d) illustrates the near-equilibrium redox behavior of gold. This CV plots the electronic current I into the WE versus the overpotential η of the WE. A positive current indicates a positive charge flow into the WE. The overall redox reaction is



The overpotential is defined as $\eta = V_{\text{App}} - V_{\text{Eq}}$ where V_{App} is the applied potential, and V_{Eq} is the equilibrium potential at which no current flows. This CV was collected using essentially identical, gold working, reference, and counter-electrodes in 5.0 mM KAuCl_4 (aq) solution. Equation (1)

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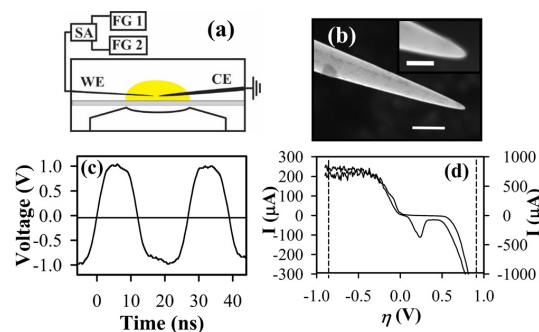


FIG. 1. (a) Side-view of experimental set-up. FG 1 and FG 2 denote the function generators; SA denotes a summing amplifier. (b) Scanning electron micrograph of a gold WE. Scale bar = $1.0\ \mu\text{m}$. *Inset*: enlarged view of tip. Scale bar = $200\ \text{nm}$. (c) Square-wave voltage signal used to grow gold nanoribbons. (d) Cyclic voltammogram of aqueous $5\ \text{mM}\ \text{KAuCl}_4$ solution, measured with gold WE, RE, and CE. Dashed lines indicate a typical square-wave amplitude in DENA. Scan rate = $10\ \text{mV/s}$.

runs forward (deposition) when a negative overpotential is applied and runs backwards (dissolution) when a positive overpotential is applied. The negative current drops sharply near $+0.25\ \text{V}$, indicating that dissolution ceases.¹⁶ This behavior is attributed to passivation of the WE interface.¹⁶ More positive overpotential values have a little effect until water-oxidation begins near $\sim 0.80\ \text{V}$. Hence, the redox electrochemistry of gold (Equation (1)) is asymmetric: negative overpotentials $< -0.25\ \text{V}$ induce deposition whereas positive overpotentials $> +0.25\ \text{V}$ do *not* induce comparable levels of dissolution.

Figure 2(a) is an optical micrograph of a gold ribbon that was grown by the DENA method with a $37.0\ \text{MHz}$ square wave of amplitude $0.88\ \text{V}$. The ribbon is $261\ \mu\text{m}$ long and branchless. A movie showing its growth is available online (Multimedia view). The $0.88\ \text{V}$ amplitude used to grow this nanoribbon is indicated by the vertical dashed lines at $\pm 0.88\ \text{V}$ in the CV of Figure 1(d). This comparison suggests that during DENA, the negative half cycle crystallizes gold whereas the positive half cycle has little effect (due to passivation¹⁶); hence, a full cycle causes net deposition.

Some caution is warranted here as a conventional CV may not reflect the non-equilibrium behavior driven by a RF voltage. A scanning electron microscope (FEI Versa 3D Dual Beam) equipped with an energy dispersive X-ray spectrometer was used to characterize the $2.7 \times 2.7\ \mu\text{m}^2$ sample of a nanoribbon on ITO-coated glass, shown in the inset of Figure 2(a). Weight-percentages of 3.9% Au, 38.6% O, 30.3% Si, 6.2% Na, 10.3% In, and 3.0% Sn were observed, as well as trace quantities of Mg, K, Ca, and Al. The Au and O fluorescence maps [*insets*, Figure 2(a)] show that the Au signal correlates with the ribbon-location whereas the O signal anti-correlates with the ribbon-location, suggesting that the ribbon is composed of gold. The O, Si, Na, In, and Sn content are attributed to the substrate.

The ribbon-like nature of these nanostructures is evident in the scanning electron micrographs in Figures 2(b)–2(d). The widths of these (and 8 other) samples are between $130\ \text{nm}$ and $360\ \text{nm}$. The tip-region shown in Figure 2(e) is narrower, having a lengthwise averaged diameter of $58 \pm 3\ \text{nm}$, and the foremost tip width is $\sim 10\ \text{nm}$ (*inset*). The thickness of these ribbon-like wires was characterized by atomic force microscopy (Veeco, di Innova). Figure 2(f) is a topographical image of a $171\ \mu\text{m}$ gold nanoribbon on a glass coverslip. (This image is a composite 8 overlapping images of the wire). Figure 2(g) compares the topographical profile of the spine of the ribbon to that of the adjacent glass substrate. The dashed line in panel (f) indicates the location of these profiles. The difference between their lengthwise averaged heights is $37 \pm 9\ \text{nm}$, a value that is representative of the ribbon-thickness elsewhere along the structure. Hence, the length-to-thickness aspect ratio is $171\ \mu\text{m}/37\ \text{nm} \approx 4.6 \times 10^3$ for this ribbon. We have topographically examined two other nanoribbons, obtaining the average thicknesses of $44\ \text{nm}$, and $39\ \text{nm}$, demonstrating that the growth of nanoribbons with high length-to-thickness aspect ratios is feasible with this technique.

Figure 3(a) depicts an electron diffraction pattern collected from the nanoribbon shown in panel (f). This study used a $200\ \text{kV}$ electron microscope (FEI Tecnai F20 XT) that was set to a $290\ \text{mm}$ camera length and a $10\ \mu\text{m}$ diameter area selection aperture. Figure 3(b) shows the simulated

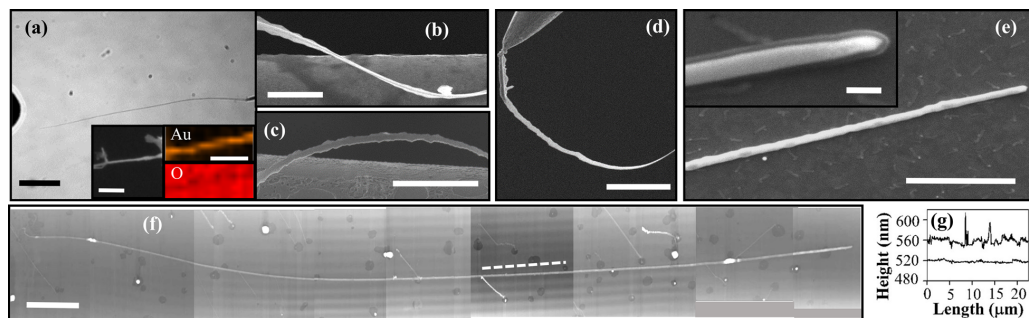


FIG. 2. (a) Optical image of a gold nanoribbon grown with a voltage amplitude of $0.88\ \text{V}$ for $304\ \text{s}$. Scale bar = $50\ \mu\text{m}$. A video of this event is available online. *Inset*: SEM micrograph of a nanoribbon (left panel, Scale bar = $1\ \mu\text{m}$) and X-ray fluorescence maps of same segment showing locations of Au and O (as labeled, Scale bar = $500\ \text{nm}$). (b)–(d) Scanning electron micrographs of curved nanoribbon segments, displaying their ribbon-like shape. Scale bars = $1\ \mu\text{m}$, $2\ \mu\text{m}$, and $2\ \mu\text{m}$, respectively. (e) Scanning electron micrograph of tip region of nanoribbon. Scale bar = $1\ \mu\text{m}$. *Inset*: Enlarged view of tip region. Scale bar = $100\ \text{nm}$. (f) Composite topographical image of a $\sim 171\ \mu\text{m}$ long gold nanoribbon. Scale bar = $10\ \mu\text{m}$. (g) Height profiles collected from the spine of the nanoribbon and the adjacent substrate near the region indicated by the white dashed line in panel (f). (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4976027.1>]

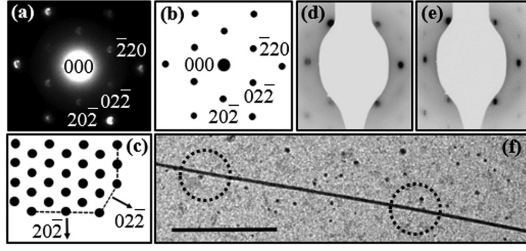


FIG. 3. (a) Selected area electron diffraction pattern of the nanoribbon shown in panel (f). (b) Simulated electron diffraction pattern of single crystalline gold viewed along the [111] zone axis. (c) Real space schematic corresponding to the pattern shown in panel (a). (d) and (e) Diffraction patterns collected from the nanoribbon-regions marked by the circles in panel (f). (f) Transmission electron micrograph of a gold nanoribbon. Scale bar = 20 μm .

pattern (calculated with CSpot 1.2.0) for face centered cubic gold ($Fm\bar{3}m$ space group) with lattice parameters of $a = b = c = 0.40786 \text{ nm}$, viewed along the [111] zone axis.¹⁷ The measured and simulated patterns are in excellent agreement, confirming the gold composition of the ribbon. Figure 3(c) is an atomic-level schematic of the (111) surface, corresponding to the orientation in panel (a). Figures 3(d) and 3(e) depict the selected area electron diffraction patterns that were collected from the sites indicated by the circles in panel (f). (A beam stop blocks the 000 spot and the first ring of spots in these patterns). The six spots in both of the patterns are identically oriented. The invariant positions of the spots indicate that the crystal structure of this nanoribbon does not change along the 46 μm length that was examined in this study. A similar result was observed with electrochemically grown gold nanowires.⁹

Ribbon growth is difficult to induce with voltage amplitudes less than 0.750 V whereas larger amplitudes not only cause increasingly rapid growth but also enhance the likelihood of side-branching. Samples grown at the same frequency (37.0 MHz) but with amplitudes ranging from 1.05 V to 1.5 V are shown in Figures 4(a)–4(c), respectively. The degree of side-branching increases significantly across this range. The distances between adjacent branches in panels (a)–(c) lie in the 1.1 to 8.2 μm range. Thermal noise is a commonly cited cause of side-branching in the dendritic crystallization of super-cooled melts.^{18–20} To see if electrical noise induces side-branching in electrochemical dendritic growth, we have used a summing amplifier to add 800 mV of 20 MHz bandwidth-limited white noise to the 37.0 MHz square wave that was used to drive nanoribbon growth. The inset to Figure 4(d) shows the 1.0 V square wave (dashed line), the 800 mV white-noise (dotted line), and the combined signal (solid line). Figure 4(d) shows a nanoribbon that was grown using the square wave alone. The noise component was then added. Figure 4(e) was collected $\sim 20 \text{ s}$ later, showing the branched structure that developed in response to the added noise. The arrow indicates the tip position when the noise was added. A movie depicting the growth of this structure is available online (Multimedia view). A null effect was observed when only noise (up to 1.7 V) and no square wave signal was applied. These data show that excess electrical noise induces side-branching, and, consequently, can

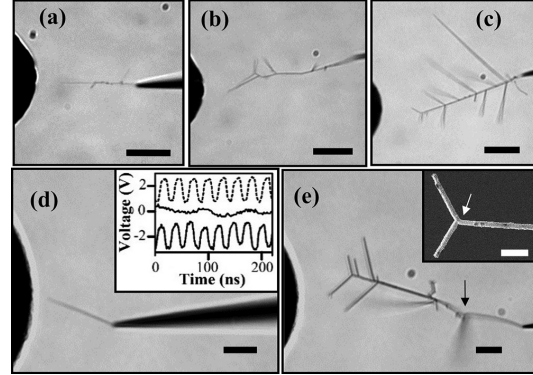


FIG. 4. (a) Optical images of gold dendrites grown with amplitudes of (a) 1.05 V for 79 s; (b) 1.2 V for 59 s; and (c) 1.5 V for 16 s. Scale bars = 20 μm . (d) Optical image of a gold nanoribbon grown with a square wave, as for Figure 2(a). Scale bar = 10 μm . Inset: 37.0 MHz square wave (dashed line), noise (middle solid line), and combined (lower solid line) voltage signals. Vertical offsets were added to separate the profiles. (e) Optical image of the nanoribbon after application of the square wave + noise signals. The arrow denotes the point at which the noise was turned on. Scale bar = 10 μm . A video of this event is available online. Inset: Y-shaped structure grown by applying a noise pulse. Scale bar = 2 μm . (Multimedia view) [URL: <http://dx.doi.org/10.1063/1.4976027.2>]

be used to tailor the morphology. For example, the Y-shaped structure in the inset, of potential interest for studying surface plasmon-propagation through a junction, was grown by applying a $\sim 4 \text{ s}$ pulse of noise at the designated point.

Direct measurement of the current during the (13.5 ns) negative half-cycles is challenging as only a few atoms join the crystal during this period. Instead, we have estimated the current density associated with deposition (i.e., the Faradic current density) by observing the nanoribbon growth velocity. Figure 5(a) plots the average growth velocity $\langle v \rangle$ (unfilled circles) versus the voltage amplitude. Mass conservation implies that growth at velocity $\langle v \rangle$ requires an average current density of

$$\langle j \rangle \cong ze\rho_{Au}\langle v \rangle, \quad (2)$$

where $\rho_{Au} = 5.89 \times 10^{28} \text{ m}^{-3}$ is the number density of gold, and ze (where $z = 3$) is the charge that is transferred during a step of Equation (1). These values (filled circles) are given by the right axis in Figure 5(a). The current density increases

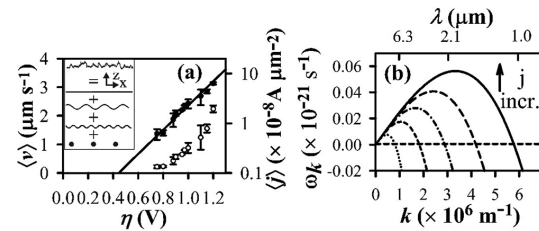


FIG. 5. (a) Growth speed (unfilled circles) and Faradic current density (filled circles) versus the amplitude of the alternating voltage signal. *Fit parameters:* $T = 300 \text{ K}$; $c_O = 0.6 \times c_O^*$; $c_O^* = 40 \text{ mM} = 2.41 \times 10^{25} \text{ m}^{-3}$; $\rho_M = 5.89 \times 10^{28} \text{ m}^{-3}$; $\gamma = 100 \text{ J m}^{-2}$; $\kappa = (30 \times 10^{-9} \text{ m})^{-1}$. Inset: schematic of a rough interface decomposed into its Fourier modes. (b) Amplification rate versus wave vector for five arbitrarily chosen j -values.

sharply with amplitude beyond a threshold of ~ 750 mV. This plot is essentially a *non-equilibrium* voltammogram for gold reduction during DENA. To model this process, we assume that the overall deposition process (Equation (1)) is rate-limited by a single-electron step of the form $O^z + e^- = R^0$, where O^z is a gold species in the $z = 1$ oxidation state, and R^0 is the rate-limited product. The Butler-Volmer equation relates the current density collected by an electrode to the overpotential η ²¹

$$j = j_0 \left[\frac{c_O}{c_O^*} e^{-\alpha\beta \left(e\eta - \frac{1}{\beta} \ln \frac{c_O}{c_O^*} + \rho_{Au}^{-1} \gamma \kappa \right)} - e^{(1-\alpha)\beta \left(e\eta - \frac{1}{\beta} \ln \frac{c_O}{c_O^*} + \rho_{Au}^{-1} \gamma \kappa \right)} \right], \quad (3)$$

where η is defined above. α is the symmetry factor associated with the energy barrier to reduction, and β is the inverse thermal energy $(k_B T)^{-1}$. c_O (c_O^*) is the interfacial (bulk) concentration of species O^z . The Gibbs-Thomson factor $\rho_{Au}^{-1} \gamma \kappa$ accounts for curvature effects.²² γ is the surface tension of the gold-solution interface, and κ is the local curvature of the interface defined such that a protrusion (depression) has a positive (negative) curvature. The solid line in Figure 5(a) is a best-fit of Equation (3) to the estimated current density data. An exchange current density of $j_0 \sim 1100$ A m⁻² and symmetry factor $\alpha = 0.145$ are needed to account for the ~ 750 mV threshold to charge flow. The other fitting parameter-values are reported in the caption. The fit-quality is reasonably good, indicating that the Butler-Volmer model accurately describes the high frequency (37 MHz) gold reduction that occurs during the DENA process.

A linear stability analysis by Haataja and co-workers illustrates how electrochemical systems that obey Equation (3) can become unstable and undergo side-branching.²¹ A microscopically rough interface is sketched in the inset to Figure 5(a). Let this interface represent a profile of the nanoribbon, like that in Figure 2(g). This profile $z(x, t)$ may be decomposed into a sum of Fourier modes, each of spatial frequency k (units: rad/m), a few of which are sketched in the inset. The contribution of a single mode is $z + \delta z_k(x, t) = vt + \delta z_{0,k} e^{ikx} e^{\omega_k t}$. v is the steady-state growth velocity of the interface in the z -direction, and $\delta z_{0,k}$ is the amplitude of the k th mode. The factor $e^{\omega_k t}$ is the stability factor. If the surface is stable, the amplification rate ω_k (for each mode) is equal to zero, but for an unstable surface ω_k is non-zero. If ω_k is positive (negative), mode k will experience amplified (retarded) growth. If, for example, all modes other than k are stable, the nanoribbon-profile will become wave-like (with spatial wavelength $\lambda = 2\pi/k$), and the crests of the wave will become side-branches. This effect occurs because a protrusion on a surface steepens the local solute concentration gradient and, thereby, increases the local current density and the growth rate of the protrusion. This feedback mechanism is known as the Mullins-Sekerka instability.²³ Time-differentiation of $z + \delta z_k$ gives the growth velocity of the k th mode: $v + \delta v_k = v + \omega_k \delta z_k$. Growth at velocity $v + \delta v_k$ requires a current density $j + \delta j_k \cong ne\rho_{Au}(v + \delta v_k)$, where Equation (2) was used. Substituting $\omega_k \delta z_k$ for δv_k gives the current density fluctuation, which is a measure of the electrical noise level

$$\delta j_k(x, t) = ne\omega_k \rho_{Au} \delta z_k. \quad (4)$$

Hence, the noise-level δj_k and the amplification rate ω_k are proportional to each other, implying that elevated noise levels can amplify the growth rate of the protrusions.

For a roughened but flat electrochemical interface, Haataja and co-workers²¹ have derived a dispersion relation for ω_k : (Equation 16 in Ref. 21)

$$\omega_k \cong \frac{\bar{j}k \left[\bar{j}(1 + \alpha) - \left(\frac{3}{2} - \bar{j} \right) \hat{\gamma} \alpha k^2 \right]}{\rho_{Au} \left[\bar{j}(1 + \alpha) + \left(\frac{3}{2} - \bar{j} \right) k \right]}, \quad (5)$$

where the unitless current density is $\bar{j} = \frac{j}{j_0}$ and $j_0 = \frac{neDc_O^*}{L_\infty}$. This function is plotted for five experimentally realized j -values (near 4.9×10^{-8} A μm^{-2}) in Figure 5(b). To attain these plots, the diffusion coefficient of gold chloride was estimated to be $D \sim 1.0 \times 10^{-9}$ m² s⁻¹, and a value of $L_\infty = 3.5 \times 10^{-6}$ m was used for the diffusion length, giving $j_0 \cong 3306$ A m⁻². These plots show that ω_k is positive for finite ranges of k -values, denoting the unstable modes. Moreover, the magnitude of ω_k across these unstable regions increases with j . Hence, larger voltage amplitudes V_{App} , which drive larger current densities j [by Equation (3)], are expected to induce stronger degrees of side-branching. Thus, an upsurge in either the amplitude V_{App} or the noise δj_k will inflate the amplification rate ω_k and induce side-branching. This picture explains our main observations: that minimal voltage amplitudes are required to suppress side-branching, and that excess noise tends to induce it (Figure 4). A more quantitative analysis will benefit from direct measurement of the deposition current density and a 3D theory that addresses the cylindrical geometry and, possibly, surface tension anisotropy of the crystalline nanoribbon.

In conclusion, we report the methodology for the electrochemical growth of ultra-long, branchless gold nanoribbons. Their fabrication is enabled by the use of sharp, electroetched working electrodes that permit wire growth with voltage amplitudes in the 0.75–1.0 V range. Reduced amplitudes induce no growth, possibly due to the nearly reversible redox chemistry of gold at low amplitudes, whereas elevated amplitudes, or excess electrical noise, strongly enhance the degree-of side-branching. Collectively, these results illuminate the relationship between voltage amplitude, electrical noise, and side-branch formation during electrochemical dendritic growth and illustrate how side-branching may be controlled. The fabrication of long, branchless nanoribbons is one application. It is also possible to add noise in a controlled manner in order to fabricate nanoribbons with branches at selected points along the main trunk—another structure of optoelectronic interest. Finally, the common effect (side-branch formation) that amplitude and noise cause suggests that *shot noise*, which scales with amplitude, may be an important factor in the DENA process. This possibility will be examined in the future.

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Appendix C

Conducting polymer nanowires for control of local protein concentration in solution

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Conducting polymer nanowires for control of local protein concentration in solution

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Abstract

Interfacing devices with cells and tissues requires new nanoscale tools that are both flexible and electrically active. We demonstrate the use of PEDOT:PSS conducting polymer nanowires for the local control of protein concentration in water and biological media. We use fluorescence microscopy to compare the localization of serum albumin in response to electric fields generated by narrow (760 nm) and wide (1.5 μ m) nanowires. We show that proteins in deionized water can be manipulated over a surprisingly large micron length scale and that this distance is a function of nanowire diameter. In addition, white noise can be introduced during the electrochemical synthesis of the nanowire to induce branches into the nanowire allowing a single device to control multiple nanowires. An analysis of growth speed and current density suggests that branching is due to the Mullins–Sekerka instability, ultimately controlled by the roughness of the nanowire surface. These small, flexible, conductive, and biologically compatible PEDOT:PSS nanowires provide a new tool for the electrical control of biological systems.

Keywords: PEDOT:PSS, polymer nanowires, conductive polymers

 Supplementary material for this article is available [online](#)

(Some figures may appear in colour only in the online journal)

1. Introduction

The basic components of biological systems are small, ranging from nanometer-scale proteins to micron-sized cells, and soft. For example, the Young's modulus of neural tissue is 100 kPa–1000 kPa [1, 2]. The small size and soft materials of human biology provide a challenge for the use of implantable bioelectric devices such as neural electrodes [3–5]. The mismatch between the stiffness of implanted materials and

the softness of cells and tissues leads to cellular damage and elicits an immune response. Soft materials, such as polymers and hydrogels, are more biocompatible with a Young's modulus comparable to tissue. However, materials used at the bioelectric interface need to be electrically conductive, as well as small and flexible.

Electrically conductive polymer nanowires, described previously [6–8], provide a small, flexible, electrically active material for the bioelectric interface. Poly(3,4-ethylenedioxythiophene):polystyrene sulfonate (PEDOT:PSS) nanowires are of specific interest due to the extensive characterization

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and known biocompatibility of PEDOT:PSS [9–14]. These nanowires have been electrochemically synthesized with average diameters of 340 nm, a Young's modulus of ~ 1 GPa, and conductivity of $\sim 8.0 \text{ S cm}^{-1}$ [6–8, 15]. Although the PEDOT:PSS nanowires are still stiffer than cells or tissue, they are two orders of magnitude more flexible than current state-of-the-art carbon fiber neural electrodes with a diameter of $4.5 \text{ }\mu\text{m}$ and a Young's modulus of 380 GPa [16].

Conducting polymer nanowires are promising tools for controlling the local concentrations of charged molecules, including proteins, at cellular and subcellular length scales. Previous work has demonstrated the use of conductive polymer films to control the concentration of proteins in solution [17]. In this work, we demonstrate the use PEDOT:PSS nanowires, rather than bulk films, to control the local concentration of proteins in solution. We compare localization of charged proteins in response to electric fields generated by narrow (760 nm) and wide ($1.5 \text{ }\mu\text{m}$) nanowires. We show that proteins in deionized water can be manipulated over a surprisingly large micron length scale through the application of an electric field. We then compare this to an electric field applied in a high salt biological media, phosphate buffered saline (PBS). For future biological applications, which are likely to require multiple nanowires rather than a single nanowire, we demonstrate the synthesis of branched nanowires, allowing a single device to control multiple nanowires.

2. Experimental details

2.1. Electrochemical synthesis of PEDOT:PSS nanowires

Conducting polymer nanowires were synthesized using directed electrochemical nanowire assembly in which nanowires are electropolymerized between two sharp gold electrodes [6–8, 18]. Sharpened gold electrodes were fabricated by adapting methods used to etch scanning tunneling microscope electrodes [19]. Briefly, solid gold wire (0.2 mm diameter, 99.9%, Alfa Aesar, 10195-G1) was secured to 20 gauge stranded wire using parafilm. Gold wires were submersed ~ 1 mm in high-concentration hydrochloric acid (6 M). Coiled platinum wire (0.3 mm diameter, 99.9%, Alfa Aesar, 43014-BU) served as the counter-electrode. A function generator (Agilent 33120A) provided a 10 Hz full square wave, $\pm 5 \text{ V}$ amplitude. The square wave was rectified using a diode to deliver positive 5 V square pulses to the gold anode to initiate the reduction of gold into solution. Etching was terminated after ~ 90 s to yield tip diameters < 100 nm. After etching, electrodes were rinsed with ethanol, then water, and dried under nitrogen. Electrodes were plasma cleaned (Harrick) for 20 s before use.

PEDOT:PSS nanowires were synthesized in an aqueous solution containing 10 mM 3,4-ethylenedioxythiophene (EDOT, Sigma-Aldrich, 483028) monomer and 20 mM polystyrene sulfonate (PSS, Sigma-Aldrich, 243051) as a counterion. PEDOT:PSS nanowires were grown using a function generator (Agilent 33120A) supplying an alternating,

square-wave voltage (2–100 kHz) across two sharp gold electrodes. The length of the nanowires is controlled by the spacing of the gold electrodes. The diameter of the nanowires is controlled by the frequency of the voltage used for the electrochemical synthesis. The wider nanowires ($1.50 \pm 0.55 \text{ }\mu\text{m}$ diameter) were grown at 2 kHz and the thinner nanowires ($760 \pm 220 \text{ nm}$ diameter) were grown at 10 kHz. Nanowire diameter was measured using a scanning electron microscope (SEM, Hitachi SU8230) and are the average of 4 different nanowires. Nanowire length was measured using brightfield microscopy (Olympus IX71, $60\times$ objective, Andor iXon CCD camera). Nanowires were grown and imaged in a custom made flow cell to facilitate media exchange between the monomer solution and protein solution. Electrodes were spaced $50 \text{ }\mu\text{m}$ apart (tip-to-tip). A -100 mV DC offset voltage was applied to promote PEDOT:PSS nanowire growth from a single electrode. The gap between the counter-electrode and the end of the growing nanowire was held constant by manually adjusting one of the micromanipulators. A Raman microscope (iHR550 Horriba-Jobin Yvon spectrometer fiber-coupled to a BX-41 Olympus microscope) was used to confirm nanowire composition.

Branched nanowires were fabricated by adding a white noise voltage signal to the square wave during nanowire growth. The white noise signal was produced by a second function generator (Agilent, 3220A). A custom-designed high bandwidth summing amplifier was used to combine this wave with the square wave. To prevent attenuation of the noise signal, the amplifier bandwidth should exceed that of the white noise generator (20.0 MHz). The voltage-dependent current density, $\langle \hat{j} \rangle$, (equation (1)), is required to understand the branching of the PEDOT:PSS nanowires. Average growth velocities, $\langle v \rangle$, of the PEDOT:PSS nanowires at different voltage amplitudes were determined by analyzing movies of nanowire growth. The movies are collected at a rate of 10 Hz and were typically 100–400 s in length. Mass conservation implies that growth at velocity $\langle v \rangle$ requires an average current density of;

$$\langle \hat{j} \rangle \cong ze\rho_{\text{PEDOT}}\langle v \rangle, \quad (1)$$

where $\rho_{\text{PEDOT}} = 6.22 \times 10^{27} \text{ m}^{-3}$ is the estimated number density of EDOT monomers in the PEDOT:PSS nanowire and ze (where $z = 1$) is the charge that is transferred during the addition of one EDOT monomer to the nanowire.

The Butler–Volmer equation is commonly used to analyze the current density associated with electrochemical deposition, as occurs during PEDOT:PSS nanowire growth. This Arrhenius-type rate law characterizes the rate-limiting step of the overall chemical mechanism by which the deposition process occurs. We assume that this process is rate-limited by a single electron step of the form $R^0 = O^z + e^-$, where R^0 is the EDOT monomer and O^z is the rate-limited, oxidized EDOT species in the $z = 1$ oxidation state. The Butler–Volmer equation relates the current density collected by an electrode of curvature κ to the overpotential η [20]:

$$\hat{j} = \hat{j}_0 \left[-e^{-\alpha\beta \left(e\eta + \frac{1}{\beta} \ln \frac{c}{c_0} - \rho_{\text{PEDOT}}^{-1} \hat{\gamma} \kappa \right)} + \frac{c}{c_0} e^{(1-\alpha)\beta \left(e\eta + \frac{1}{\beta} \ln \frac{c}{c_0} - \rho_{\text{PEDOT}}^{-1} \hat{\gamma} \kappa \right)} \right], \quad (2)$$

where $\hat{j}_0$ is the exchange current density, $\eta = V_{\text{App}} - V_{\text{Eq}}$, V_{App} is the applied potential, and V_{Eq} is the equilibrium potential at which no current flows. Only the oxidation term is significant during the positive half cycles when deposition occurs. In equation (2), a positive current density corresponds to deposition and implies a net flow of negative charge into the working electrode. α describes the symmetry of the activation energy barrier along the reaction coordinate and β is the inverse thermal energy $(k_B T)^{-1}$. c (c_0) is the interfacial (bulk) concentration of EDOT. The Gibbs–Thomson factor $\rho_{\text{PEDOT}}^{-1} \hat{\gamma} \kappa$ accounts for curvature effects [21] and γ is the surface tension of the polymer–solution interface. κ is the local curvature of the interface and is defined as $\kappa \cong -\partial^2 h / \partial x^2$. A protrusion (depression) has a positive (negative) curvature and a retarded (enhanced) growth rate. The Gibbs–Thomson effect is due to the decreased (increased) degree of bonding between neighboring surface molecules on the protrusion (depression). The Gibbs–Thomson effect is counteracted by the Mullins–Sekerka instability, which enhances the deposition rate on sharp protrusions, as described in the appendix. The competition between these two effects results in branching at sufficiently high voltage amplitude, V_{App} .

2.2. PEDOT:PSS nanowire conductivity

The conductivity of the nanowire was determined using a two-point probe resistance measurement. A peristaltic pump was used to rinse the nanowire with 25 ml of deionized water to remove residual monomer. A $\pm 1\text{V}$, 10 kHz square wave was applied between the nanowire and the counter-electrode to fuse the nanowire across the electrodes. A Keithley 2400 source meter was controlled using a custom Igor Pro script to measure resistance. Voltage was swept between -1 and $+1$ V while measuring current. The resistance of the wire was determined by the inverse slope of the linear best fit line. Conductivity of the nanowire was calculated using the formula:

$$\sigma = \frac{L}{AR} \quad (3)$$

where σ is conductivity (S cm^{-1}), L is nanowire length, A is nanowire cross-sectional area, and R is electrical resistance. Two-point probe measurement were carried out on 13 nanowires.

2.3. Imaging protein concentration

To image protein localization, bovine serum albumin (BSA, Thermo Fischer Scientific, BP1600-100) was labeled with AlexaFluor546 (Thermo Fischer Scientific, A20002)

according to the manufacturer's instructions. After the growth of a nanowire, the EDOT and PSS solution was exchanged for ultrapure deionized water (EASYPure II, Barnstead) or phosphate buffered saline (PBS, Gibco, 14040). Fluorescently-labeled BSA was then added to the solution for a final volume of 1.5 ml. Fluorescence images were taken with an EMCCD camera (Andor iXon CCD camera) coupled to an inverted microscope (Olympus IX71, 40 $\times$ objective). Profile plots of fluorescence intensity within a $25 \mu\text{m} \times 10 \mu\text{m}$ box, centered on the nanowire, were used to quantify the amount of protein as a function of distance. The plots are an average of 25 line profiles taken perpendicular to the nanowire, averaging the fluorescence intensity for 20 ms at each pixel. This area was chosen to cover the full distance over which protein concentration was affected by the nanowires and to maximize the number of lines available for averaging. An average, rather than a single line profile, was used to minimize noise. The plots were generated using Igor Pro's image processing package.

3. Results

3.1. Use of PEDOT:PSS nanowires to control local protein concentration

The electrochemical synthesis of conducting polymer nanowires has been described previously [6–8]. SEM was used to measure the diameter of the nanowires (figure 1(a) and (b), supporting figure 1 (stacks.iop.org/JPhysD/50/174003/mmedia)) and nanowire composition was confirmed by comparing Raman spectra of the nanowires with a PEDOT:PSS film (figure 1(c)). Conductivity of the nanowires was measured with two-point probe resistance measurements. The average PEDOT:PSS nanowire conductivity was found to be $22 \pm 10 \text{ S cm}^{-1}$ ($n = 13$ wires). Surface roughness of the nanowires, measured as an integrated area normalized by the length of the segment measured, was 17.6 ± 8.3 and $23.4 \pm 7.8 \mu\text{m}$ for nanowires synthesized at 10 and 2 kHz, respectively (non-significant difference, p -value = 0.35, $n = 4$ nanowires at each diameter, supporting figure 1).

We first used relatively thick PEDOT:PSS nanowires with a diameter of $1.5 \mu\text{m}$ (length = $25 \mu\text{m}$) to control local protein concentration. Fluorescently-tagged BSA protein was added to the solution after nanowire growth and an AC field ($\pm 1\text{V}$, 1 Hz, square wave) was applied. Protein concentration, measured as fluorescence intensity, increased in the region of the PEDOT:PSS nanowire while a positive bias was applied (figure 2(a)). A decrease in concentration was observed at negative biases (figure 2(b)). This behavior is consistent with expectations given the net negative charge of BSA [22, 23]. To quantify the change in protein concentration as a function of distance from the nanowire, fluorescence intensity within a $25 \mu\text{m} \times 10 \mu\text{m}$ box, centered on the nanowire, was averaged over 20 ms (figure 2(c)). An oscillation in fluorescence intensity, from a high value of 182.0–188.5 a.u. to a low value of 103.9–122.9 a.u., was observed within this region in response to the electric field, applied at $t = 4$ s. To confirm that the oscillation in protein concentration is due to the nanowire, and not the gold electrode, we took line profiles of the fluorescence

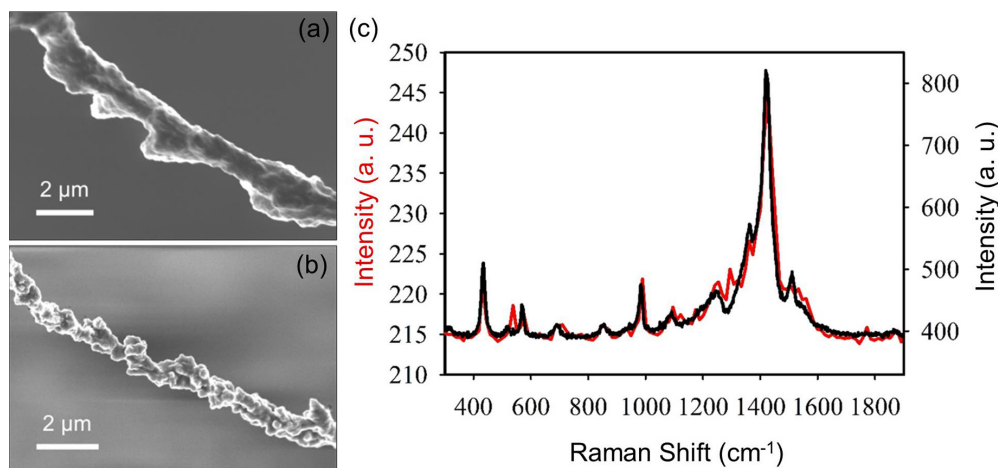


Figure 1. PEDOT:PSS nanowires. (a) SEM of a PEDOT:PSS nanowire grown with an AC frequency of 2 kHz. (b) SEM of a PEDOT:PSS nanowire grown with an AC frequency of 10 kHz. (c) Raman spectrum of a PEDOT:PSS nanowire (black), compared to a PEDOT:PSS film (red).

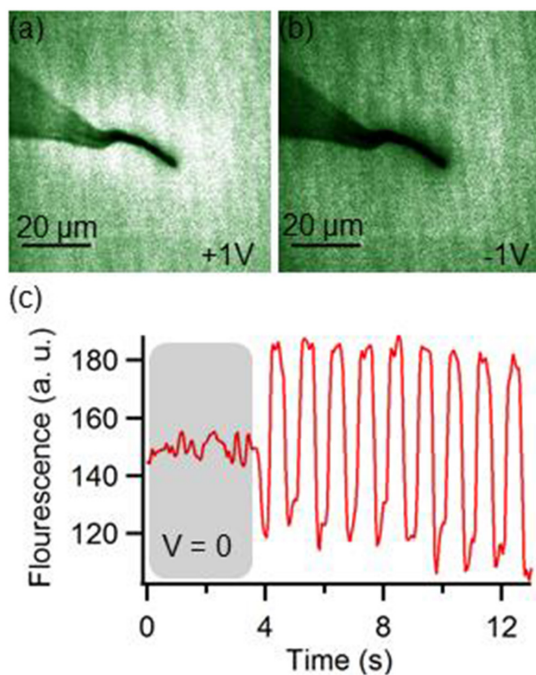


Figure 2. Representative fluorescence microscopy imaging of a PEDOT:PSS nanowire with fluorescently-labeled BSA (~100 nM) in the surrounding solution. The protein responds to an applied AC field (± 1 V, 1 Hz) from the nanowire. (a) Image of a nanowire and protein (green/bright); +1 V with respect to the gold counter-electrode. (b) Image of a nanowire and protein (green/bright); -1 V with respect to the gold counter-electrode. (c) Protein concentration, measured as fluorescence intensity, as a function of voltage in a $25 \mu\text{m} \times 10 \mu\text{m}$ region of interest surrounding the PEDOT:PSS nanowire.

intensity roughly $12 \mu\text{m}$ away from the gold electrode surface, similar to the distance used for the nanowire analysis (figure 2).

There was no significant change in fluorescence with changes in bias indicating that it is the PEDOT:PSS nanowire, not the gold electrode, responsible for altering the BSA concentration (supporting figure 2).

3.2. Comparison of protein modulation as a function of nanowire diameter

To determine the importance of nanowire diameter for controlling local protein concentration, we repeated experiments using a thinner PEDOT:PSS nanowire with a diameter of 760 nm. In order to compare the local control of BSA, we again used profile plots of fluorescence intensity as a function of distance, centered on the nanowire (figure 3). A positive bias shows less of a drop in fluorescence intensity at the nanowire compared to a negative bias due to an accumulation of BSA at the PEDOT:PSS nanowire surface. The distance over which protein concentration was modulated was found to be $29.6 \mu\text{m} \pm 8.6 \mu\text{m}$ and $16.7 \mu\text{m} \pm 2.5 \mu\text{m}$ for the wide ($d = 1.5 \mu\text{m}$) and narrow ($d = 760 \text{ nm}$) nanowires, respectively (figures 3(a) and (b)). Averages and standard deviations were determined from measurements using three separate nanowires. We next quantified the amount of protein modulated for each diameter of nanowire. The relative quantity of protein modulated by the nanowire can be obtained by integrating the difference in area under the profiles at each bias. This integration indicates that the thin nanowire manipulates $22.1\% \pm 7.3\%$ of the quantity of protein displaced by the wider nanowire.

3.3. Comparison of nanowire activity in water and biological media

The deionized water used in the experiments described above (figures 2 and 3) provides an effective model environment for studying the modulation of protein concentration with PEDOT:PSS nanowires. However, in an actual biological environment, either cellular experiments or *in vivo*

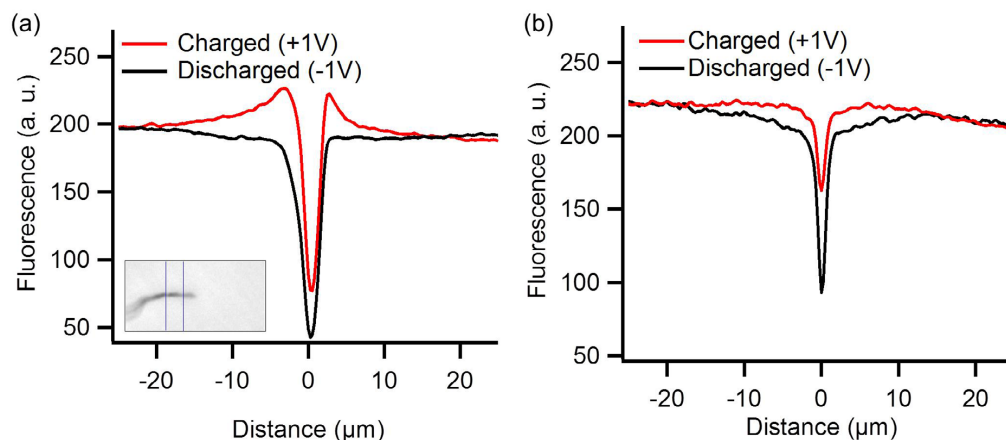


Figure 3. Representative profile plots of BSA concentration, measured as fluorescence intensity, as a function of nanowire diameter. (a) Charged (red, +1 V) and discharged (black, -1 V) PEDOT:PSS nanowire ($d = 1.5 \mu\text{m}$). The inset ($50 \mu\text{m} \times 25 \mu\text{m}$) shows the cross section of the nanowire used to generate profile plots. Profile plots are generated from an average of 25 pixel lines perpendicular to the nanowire. (b) Charged (red, +1 V) and discharged (black, -1 V) PEDOT:PSS nanowire ($d = 760 \text{ nm}$).

applications, salts will be present. For this reason, we investigated the impact of biological media on the ability to control local protein concentration using PBS, a saline solution containing sodium chloride, potassium phosphate, and sodium phosphate (150 mM total salt concentration). Similar to the experiments described above, we applied an AC field ($\pm 1 \text{ V}$, 1 Hz, square wave) to a PEDOT:PSS nanowire ($d = 1.5 \mu\text{m}$, $l = 25 \mu\text{m}$) in the presence of BSA (300 nM) in PBS. We again used profile plots to compare the spatial extent of control and find that the thickness of our electrostatic double layer drops below the resolution of our microscope (supporting figure 4).

3.4. Electropolymerization of branched PEDOT:PSS nanowires

For future biological applications, there are advantages to using multiple nanowires controlled by a single device. To this end, we have developed a method for growing multiple PEDOT:PSS nanowires from a single gold electrode. The addition of electrical noise during growth causes branches to form on the nanowire (figure 4). The number and length of the branches scales with the amplitude of the additional white noise. For example, $\sim 5 \mu\text{m}$ long branches and an average of 5 branches per nanowire at 800 mV (figures 4(e)–(h)) and 14 μm long branches and 7 branches per nanowire at 1.5 V (figures 4(i)–(l)). No growth was observed when a noise signal was applied in the absence of the square wave.

To gain insight into the branching process, we have estimated the average current density associated with the oxidative deposition of EDOT during nanowire growth. Average growth velocities, $\langle v \rangle$, of the PEDOT:PSS nanowires were measured at different amplitudes (figure 5). Velocity values were determined by analyzing movies of nanowire growth. There is a $\sim 750 \text{ mV}$ threshold to nanowire growth, below which no growth was observed. As the amplitude is increased

above this threshold, the growth velocity nonlinearly increases. Based on mass conservation (equation (1)), we convert the velocity measurements to current density values, also plotted in figure 5. Current density data are fit to the Butler–Volmer equation (equation (2)). An exchange current density of $j_0 \sim 10 \text{ A m}^{-2}$ and a symmetry factor $\alpha = 0.145$ are needed to account for the $\sim 0.75 \text{ V}$ threshold to charge flow. The other fitting parameter values are $c_R/c_R^* = 0.5$, $\gamma = 400 \text{ J m}^{-2}$ and $\kappa = R^{-1}$ where R is the 380 nm radius of the nanowire. The fit quality suggests that the Butler–Volmer model accurately describes the AC (10 kHz) EDOT oxidation that occurs during wire growth.

4. Discussion

4.1. Use of PEDOT:PSS nanowires to control local protein concentration

PEDOT:PSS nanowires have been reported with diameter of $< 500 \text{ nm}$ [6–8]. Within our lab, diameters of 500 nm– $1.5 \mu\text{m}$ are typical (figures 1(a) and (b), supporting figure 1). The length of the nanowire is controlled by the position of the two gold electrodes, typically 800 nm–10 mm. On our size scales, conductivity was found to be independent of nanowire diameter and length. Surface roughness of the nanowires, which determines the electrochemical surface area in contact with the electrolyte solution, was similar for all of the nanowires used in these experiments (supporting figure 1).

The results described above show that nanowires can be used to control the local protein concentration (figures 2 and 3). The profile plots used to quantify the amount of protein as a function of distance are representative of the behavior in the xy plane around the nanowire. The fluorescence intensity at each pixel is the sum of fluorescence in the z direction through the depth of field. For our microscope, the depth of field

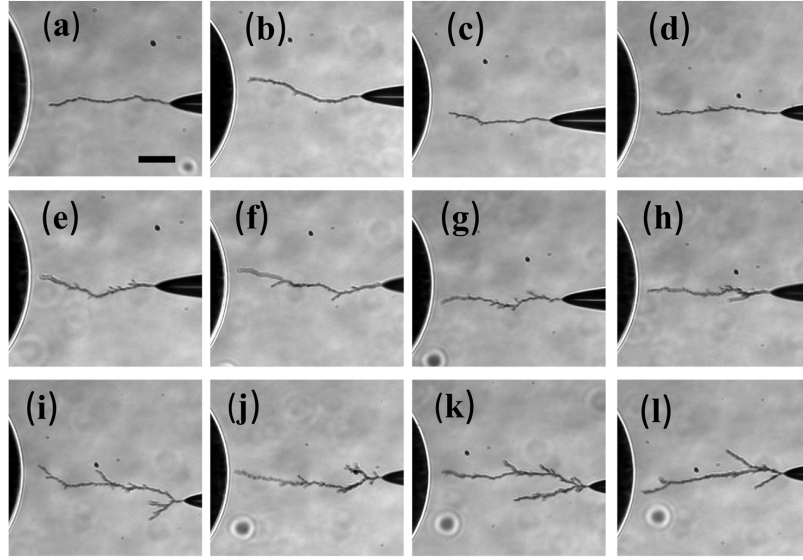


Figure 4. Brightfield images of PEDOT:PSS nanowires grown with only a square wave signal ((a)–(d), 940 mV, 10.0 kHz), with addition of white noise (800 mV) to the square wave ((e)–(h)), and an increased amplitude of white noise ((i)–(l), 1.5 V). Scale bar = 20 μm .

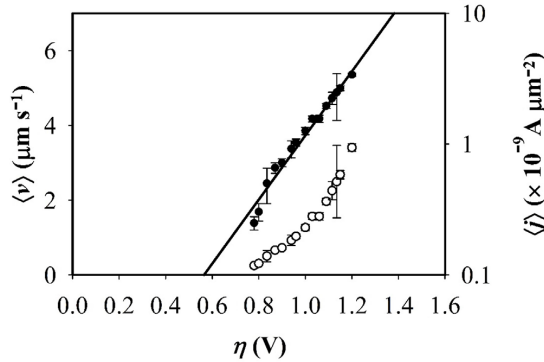


Figure 5. Growth speed ($\langle v \rangle$, unfilled circles) and mean current density ($\langle j \rangle$, filled circles) as a function of the square wave voltage amplitude. Error bars in the current density are the propagated uncertainties from the velocity for 3–5 measurements at each amplitude value. The solid line is a best-fit of equation (2) to the estimated current density data.

($\sim 1 \mu\text{m}$) is on the same scale as the diameter of the nanowires, ($\sim 750 \text{ nm}$ – $1.5 \mu\text{m}$). Given the cylindrical symmetry of the nanowires, the dominant electric field component is perpendicular to the nanowire and the dominant motion of proteins in this $1 \mu\text{m}$ slice is in the xy plane.

The distance of activity, $29.6 \mu\text{m} \pm 8.6 \mu\text{m}$ and $16.7 \mu\text{m} \pm 2.5 \mu\text{m}$ for the wide ($d = 1.5 \mu\text{m}$) and narrow ($d = 760 \text{ nm}$) nanowires, respectively, and amount of protein modulated depends on the diameter of the nanowire with the thin nanowire modulating just $22.1\% \pm 7.3\%$ of the quantity of protein displaced by the wider nanowire (figure 3, $n = 3$ for

each nanowire diameter). At equilibrium, the small nanowire would be expected to store 50% less charge due to a 50% reduction in surface area. Since BSA acts as the negatively charged species in the electrostatic double layer, this decrease in charge storage will result in the modulation of less BSA. At our frequency (1 Hz), however, the nanowires have not yet charged to equilibrium. This likely explains the deviation from the expected 50% reduction in charge storage. The increased quantity of protein manipulated by the larger nanowire highlights how altering the diameter of a PEDOT:PSS nanowire can provide the appropriate degree of charge storage for a desired application.

PBS was used as a representative biological media. In a high concentration of electrolytes, the electrostatic double layer will be comprised primarily of salts instead of BSA. In this case, we would expect the electrostatic double layer to be dramatically reduced. We find that the thickness of our electrostatic double layer drops below the resolution of our microscope for experiments in PBS (supporting figure 4). This change is expected since the diffuse layer portion of the electrostatic double layer decreases as electrolyte concentration increases [24].

It is important to note that under our experimental conditions a large number of factors that are difficult to control can alter the spatial extent over which protein is modulated. For example, slight changes in electrode geometry, changes in nanowire roughness or branching, variations in the contact resistance between the gold electrode and the nanowire, and the exact sharpness of the gold electrodes could all cause differences in the spatial extent of protein modulation. These variations are reflected in the relatively large standard deviations of the spatial extent of nanowire activity. Regardless of these factors, the most surprising aspect of this result is

the large distance over which protein is controlled for both nanowires. These distances are dramatically larger than the expected thickness of the electrostatic double layer at equilibrium, which is on the length scale of angstroms [24]. Previous reports have demonstrated ~250 nm control of proteins using electric fields [25], also much longer than expected. This previous research used fluorescence microscopy to observe the electrostatic trapping of proteins at the surface of silica. The negative zeta potential of silica (−0.25 mV) trapped the positively charged protein concanavaline A at distances up to ~250 nm. At higher ionic strength no trapping occurred, confirming the observed control was electrostatic. We show modulation of proteins over a length scale that is 100-fold greater. Conditions unique to our experiment which may alter the equilibrium thickness of the electrostatic double layer include the high curvature of the nanowire surface [26] and large counter ions (BSA) [27]. The curvature of the nanowires studied here, however, is below what is necessary to induce significant changes in the electrostatic double layer [26]. The large size of BSA is expected to increase the equilibrium electrostatic double layer, but only out to a few nanometers. Instead, we suggest that our profiles are not at equilibrium. This is possible if the nanowire is charging in a regime controlled by bulk diffusion. These slow charging times allow for variation of the concentration of electrolytes over much larger distances [28]. Experiments at lower frequencies (50 mHz) show continued charging of the PEDOT:PSS nanowire, supporting this hypothesis (supporting figure 3).

4.2. Electropolymerization of branched PEDOT:PSS nanowires

We have described a method for the synthesis of branched PEDOT:PSS nanowires (figure 4). The current density associated with nanowire growth obeys the Butler–Volmer equation (figure 5). Haataja and co-workers have recently shown how electrochemical systems that obey equation (2) may undergo branching via the Mullins–Sekerka instability [20]. We outline the mechanism here with a full discussion provided in the appendix. The surface of a PEDOT:PSS nanowire is rough on a microscopic scale (figure 1). Its roughness profile, which we will call $z(x, t)$, may be decomposed into a sum of Fourier modes, each of spatial frequency k (units: rad m^{-1}). The contribution of a single mode is $z + \delta z_k(x, t) = vt + \delta z_{0,k} e^{ikx} e^{\omega_k t}$. v is the steady-state growth velocity of the interface in the z -direction and $\delta z_{0,k}$ is the amplitude of the k th mode. The factor $e^{\omega_k t}$ is the stability factor. If the surface is unstable, ω_k is non-zero. If ω_k is positive (negative), mode k will experience amplified (retarded) growth. For example, if only mode k is unstable, the nanowire profile will become wave-like (with spatial wavelength $\lambda = 2\pi/k$). As time passes, the crests of the wave will grow into branches. This effect occurs because a protrusion on a surface steepens the local solute concentration gradient increasing the local current density and the growth rate of the protrusion (i.e. the Mullins–Sekerka instability) [29]. Time differentiation of $z + \delta z_k$ gives the growth velocity of the k th mode: $v + \delta v_k = v + \omega_k \delta z_k$. Growth at velocity $v + \delta v_k$ requires

a current density $\hat{j} + \delta \hat{j}_k \cong ne\rho_{\text{PEDOT}}(v + \delta v_k)$, where equation (1) was used. Substituting for δv_k (i.e. $\delta v_k = \omega_k \delta z_k$) gives the current density fluctuation, which is a measure of the electrical noise level:

$$\delta \hat{j}_k(x, t) = ne\omega_k \rho_{\text{PEDOT}} \delta z_k. \quad (4)$$

The noise in the current density $\delta \hat{j}_k$ and the amplification rate ω_k are proportional, suggesting that elevated noise levels induced by the applied voltage signal can increase the amplification rate and induce branching, providing a qualitative explanation for the observed noise-induced branching (figure 4).

5. Conclusion

Conducting polymer nanowires provide a tool to control the concentration of charged molecules, such as proteins, on a biologically-relevant length scale, using an applied electric field (figure 1). In deionized water, these nanowires can modulate protein concentration over ~30 μm for the wide, 1.5 μm diameter, nanowires and ~17 μm for the thinner, 760 nm diameter, nanowires (figures 2 and 3). The quantity of protein moved through solution is determined by the diameter of the nanowire, which is controlled by the frequency at which the nanowires are electrochemically synthesized. In PBS, a high salt buffer representative of a biological environment, the distance over which protein concentration can be modulated drops significantly as the thickness of the electrostatic double layer decreases (supporting figure 4). Based on our results in deionized water, we expect that protein concentration is modulated by the nanowires in PBS, but quantification of the distance will require methods beyond standard fluorescence microscopy.

We envision the use of these nanowires for cellular applications in which modulating the concentration of ions at individual cells leads to a specific cellular response. For example, to initiate action potentials in neurons through the movement of ions across the plasma membrane. A challenge for interfacing any device with any tissue is reconciling the relative softness of tissue with the stiffness of the inserted material. This mismatch in material properties leads to inflammation and scarring at the electrode, limiting the lifetime of the device and causing tissue damage [3–5, 30]. Recent work has addressed this challenge with a focus on smaller, more flexible, materials, such as ~100 nm single crystalline gold nanowires [31], softer or conformable materials [32–35], and highly sophisticated nanoelectrode arrays of metal or silicon nanoneedles, nanopillars, and nanotubes that are expected to be less invasive [36–39]. Similarly, ‘meshes’ of nanowire field-effect transistors provide both a nanoscale device for neural recording and minimize disruption during the implantation step [40, 41]. We expect that PEDOT:PSS nanowires could provide an additional tool for the modulation of single cells with minimal disruption to the surrounding tissue. Additionally, the nanowires could be used as an active material, providing both topographic and ionic control for the enhanced growth and migration of excitable cells (neurons, heart cells, muscle cells) [42–46], which have

been shown to respond to an applied electric field [47–50]. As with neural probes, a soft polymer substrate would provide a better interface for cells. For these cellular applications, it will be useful to have multiple nanowires to control multiple cells. Our results demonstrate that white noise can be introduced during the electrochemical synthesis of the nanowire to induce branches into the nanowire (figures 4 and 5). We expect these small, flexible, conductive, and biologically-compatible PEDOT:PSS nanowires will provide a new tool for the electrical control of biological systems.

Acknowledgments

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Appendix

Branching in systems that grow by dendritic solidification, as is the case for the PEDOT:PSS nanowires, is due to the Mullins–Sekerka instability [51]. Hataaja and co-workers have described how the Mullins–Sekerka instability occurs during the electrochemical reduction and deposition of metals. Here we apply this theory to PEDOT:PSS nanowire growth, which occurs by oxidative deposition of the neutral EDOT moiety. The basic concept underlying this electrochemical version of the Mullins–Sekerka instability is that the roughness of the nanowire–solution interface perturbs the EDOT concentration in solution which, in turn, perturbs the local growth rate of the interface. For this reason, the interface grows non-uniformly with the sharpest protrusions experiencing the steepest concentration gradients at their tips. These features would then undergo runaway growth, but the Gibbs–Thomson effect, which slows the growth rate of sharp protrusions, acts to balance the diffusive instability.

The basic picture is of a working electrode immersed in a salty solution containing the neutral EDOT monomers. These monomers diffuse to the electrode–solution interface where they undergo oxidative charge transfer and polymerize on the electrode surface. Conservation of the EDOT species in the solution is expressed by a continuity equation of the form:

$$\frac{\partial c}{\partial t} + \nabla \cdot j_i = 0 \quad (\text{A.1})$$

where c is the EDOT concentration. The EDOT flux j (units: particles $\text{m}^{-2} \text{s}^{-1}$) is given by

$$j = -D \nabla c \quad (\text{A.2})$$

where D is the EDOT diffusivity. The spatial and temporal dependence of the quantities c and j is implied. Equations (A.1) and (A.2) must be solved subject to appropriate boundary conditions in order to determine the concentration and flux profiles near an electrochemical interface. A key result of the Hataaja study (p C702 of [52]) is that for a perfectly flat

(unperturbed) interface, the steady state building block concentration c^{ss} is found to be approximately

$$c^{\text{ss}}(z) \cong c_0 - \frac{jL}{D} + \frac{jz}{D} \quad (\text{A.3})$$

where c_0 is the bulk cation concentration and j is the metallic cation flux onto the surface. In this case, the surface will grow steadily in time in the $+z$ direction with velocity v . We apply equation (A.3) to the present analysis of EDOT monomers near an interface.

Equation (A.3) describes the concentration profile near a perfectly flat interface. When the surface is rough, however, the surface can grow unstably. The profile of the surface may be expressed as a Fourier sum given by $h(x, t_0) = vt + \sum_k \delta z_k(x, t)$, where v is the steady-state growth velocity of the interface in the z -direction and $\delta z_k(x, t)$ is the k th oscillatory perturbation (i.e. Fourier mode) to the flat interface. The basic question regarding how the surface changes in time may be resolved by performing a linear stability analysis. In this approach, the form of $\delta z_k(x, t)$ is $\delta \hat{z} e^{ikx} e^{\omega_k t}$, where $\delta \hat{z}$ is the initial amplitude of the k th oscillatory mode. The logic of this choice is as follows. For simplicity, we will treat the surface as 1D. It is convenient to consider just the k th mode $h_k = vt + \delta z_k(x, t) = vt + \delta \hat{z}_k(t) e^{ikx}$. $\delta \hat{z}_k(t)$ is the amplitude of the k th mode, whose time dependence is (as yet) unknown. The time derivative of $\dot{h}_k$ is $\dot{h}_k = v + \delta \dot{z}_k$. We regard $\dot{h}_k$ as a function of $h_k(x, t)$ and write $\dot{h}_k = f(h_k) = f(z_0 + \delta z_k)$. To first order in the perturbation δz_k , a Taylor expansion about

z_0 yields $f(h_k) \cong f(z_0) + \delta z_k \left[\frac{df}{dh_k} \right]_{z_0}$. Equating terms between this expression and $\dot{h}_k = v + \delta \dot{z}_k$ (above) yields the differential equation $\delta \dot{z}_k = \omega_k \delta z_k$, where $\omega_k \equiv \left[\frac{df}{dh_k} \right]_{z_0}$. This equation may be solved to give $\delta z_k(x, t) = \delta \hat{z} e^{ikx} e^{\omega_k t}$, as stated above.

Sharp protrusions on a rough surface are described by highly oscillatory, large k -modes. Here we show that such protrusions experience enhanced growth rates. Equation (A.1) reduces to the diffusion equation $\nabla^2 c_k \cong 0$ if c_k is nearly stationary. We expect the rough surface to perturb the EDOT concentration in the adjacent solution and write the perturbed concentration as $c_k(x, t) = c^{\text{ss}} + \delta c_k(x, t)$, where $\delta c_k(x, t)$ is the roughness-induced concentration perturbation. By substituting this expression and equation (A.3) for c^{ss} into $\nabla^2 c_k \cong 0$, we obtain $\nabla^2 \delta c_k \cong 0$. The solution $\delta c_k(x, t) = \delta \hat{c} e^{ikx - kz + \omega_k t}$, where $\delta \hat{c}$ is the (unknown) amplitude of the k th mode of the concentration perturbation, satisfies $\nabla^2 \delta c_k \cong 0$, so we use this form for the concentration perturbation. The EDOT flux onto the interface is given by equation (A.2): $j_k \cdot \hat{n} = -D_C \nabla c_k \cdot \hat{n}$, where $\hat{n}$ is the surface normal. Making the substitutions $j_k = j_0 + \delta j_k$, $\nabla \equiv \hat{i} \frac{\partial}{\partial x} + \hat{k} \frac{\partial}{\partial z}$, $c_k = c^{\text{ss}} + \delta c_k$, and $\hat{n} = \left(-\frac{\partial h}{\partial x}, 1 \right)$ yields the result

$$\delta j_k \cong k D \delta c_k. \quad (\text{A.4})$$

This result says that modes of large k , which describe surface protrusions of large curvature, experience larger fluxes (i.e. larger δj_k contributions), than do modes of small k , which

describe surface features of small curvature. Because the flux onto the sharp features is enhanced, so is their growth rate.

The diffusive flux in solution must be equivalent to the interfacial current density $\hat{j}$ (units: $\text{C m}^{-2} \text{s}^{-1}$) described by equation (2), the Butler–Volmer equation. The relationship between j and $\hat{j}$ is $\hat{j} = ej$ where e is the electronic charge, for the single electron oxidation under consideration here. These two descriptions of the current flux can be combined to obtain an expression for the instability parameter ω_k , which dictates whether mode k will be unstable, as explained above. Making the substitutions $\hat{j}_k = \hat{j} + \delta\hat{j}_k$ and $c_k = c^{\text{ss}} + \delta c_k$ into equation (2), where we have kept only the oxidative term, yields:

$$\hat{j} + \delta\hat{j}_k = \hat{j}_0 \left[\left(\frac{c^{\text{ss}} + \delta c_k}{c_0} \right)^{1+\alpha} e^{\alpha\beta(e\eta - \Omega\gamma\kappa)} \right], \quad (\text{A.5})$$

where $\Omega = \rho_{\text{PEDOT}}^{-1}$. Evaluation of equation (A.3) on the rough surface $c^{\text{ss}}(z = \delta z_k) = c_{\delta z_k}^{\text{ss}}$ yields $c_{\delta z_k}^{\text{ss}} \cong c_0 - \frac{jL}{D} + \frac{j\delta z_k}{D} = c_0^{\text{ss}} + \frac{j\delta z_k}{D}$, where $c^{\text{ss}}(z = 0) = c_0^{\text{ss}} = c_0 - \frac{jL}{D}$. Substitution of this result; $\kappa \cong -\frac{\partial^2 h_k}{\partial x^2} = k^2 \delta z_k$; and $\hat{\gamma} = \beta\gamma\Omega$ into equation (A.5) gives:

$$\hat{j} + \delta\hat{j}_k \cong \hat{j}_0 \left(\frac{c_0^{\text{ss}}}{c_0} \right)^{1+\alpha} e^{\alpha\beta e\eta} \left[\left(1 + \frac{j\delta z_k}{Dc_0^{\text{ss}}} + \frac{\delta c_k}{c_0^{\text{ss}}} \right)^{1+\alpha} (1 - \alpha k^2 \hat{\gamma} \delta z_k) \right], \quad (\text{A.6})$$

where $\hat{\gamma} = \beta\gamma\Omega$ and the exponential factor $e^{-\Omega\gamma\kappa}$ was linearized. Using the approximation $(1 + a)^b \cong 1 + ab$ allows:

$$\hat{j} + \delta\hat{j}_k \cong \hat{j}_0 \left(\frac{c_0^{\text{ss}}}{c_0} \right)^{1+\alpha} e^{\alpha\beta e\eta} \left[\left[1 + (1 + \alpha) \left(\frac{j\delta z_k}{Dc_0^{\text{ss}}} + \frac{\delta c_k}{c_0^{\text{ss}}} \right) \right] [1 - \alpha k^2 \hat{\gamma} \delta z_k] \right]. \quad (\text{A.7})$$

Keeping only terms up to first order in the perturbations δz_k and δc_k yields:

$$\hat{j} + \delta\hat{j}_k \cong \hat{j} \left[1 + (1 + \alpha) \left(\frac{j\delta z_k}{Dc_0^{\text{ss}}} + \frac{\delta c_k}{c_0^{\text{ss}}} \right) - \alpha k^2 \hat{\gamma} \delta z_k \right], \quad (\text{A.8})$$

where $\hat{j}$ has been equated to $\hat{j}_0 \left(\frac{c_0^{\text{ss}}}{c_0} \right)^{1+\alpha} e^{\alpha\beta e\eta}$, denoting the steady state flux. The current density fluctuation $\delta\hat{j}_k$ is:

$$\delta\hat{j}_k \cong \hat{j} \left[(1 + \alpha) \left(\frac{j\delta z_k}{Dc_0^{\text{ss}}} + \frac{\delta c_k}{c_0^{\text{ss}}} \right) - \alpha k^2 \hat{\gamma} \delta z_k \right], \quad (\text{A.9})$$

which is a function of the quantities δz_k , δc_k , and $\delta\hat{j}_k$. This expression for the strength of the charge transfer perturbation scales with $-k^2$, and thus decreases with increasing k . This

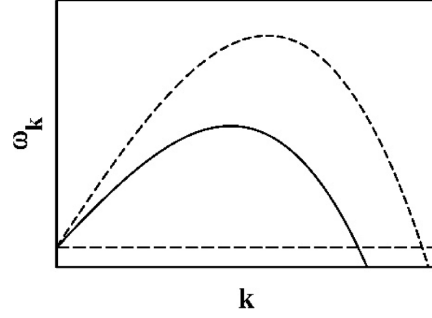


Figure A1. Plots of the instability factor ω_k versus k for a small (solid line) and large (dashed line) value of j .

result contrasts with that of equation (A.4) for the diffusive flux perturbation whose strength is proportional to k . These counteracting effects give rise to a range of k -modes that are unstable. This competition underlies branching.

To obtain an expression for ω_k that will define the k -range of unstable surface modes, we recognize that mass conservation requires the diffusive flux and current density must be equivalent and use equation (A.4) to substitute for $\delta\hat{j}_k$ in equation (A.9). We also use $c_0^{\text{ss}} = c_0 - \frac{jL}{D}$ and obtain:

$$\delta c_k \cong \frac{j \left[(1 + \alpha) \frac{j}{D} - (c_0 - jL/D) \alpha \hat{\gamma} k^2 \right]}{[j(1 + \alpha) + D(c_0 - jL/D)k]} \delta z_k. \quad (\text{A.10})$$

Mass conservation further requires that $j_0 + \delta j_k = \rho(v + \delta j_k) = \rho(v + \omega_k \delta z_k)$, so $\delta j_k = \omega_k \delta z_k$, and as $\delta j_k \cong kD \delta c_k$, we obtain $\delta c_k = \frac{\omega_k}{kD} \delta z_k$. On substituting this expression for δc_k we obtain the recursion relation that defines the instability factor ω_k :

$$\omega_k \cong \frac{j \left[(1 + \alpha) \frac{j}{D} k - Dc_0(1 - jL/Dc_0) \alpha \hat{\gamma} k^3 \right]}{[j(1 + \alpha) + Dc_0(1 - jL/Dc_0)k]} \Omega. \quad (\text{A.11})$$

As the first term in equation (A.11) increases with k and the second term decreases, there is a finite range of k -values for which ω_k is positive, as shown in figure A1. Therefore, modes with wavelengths of $2\pi/k$, where the k fall in the unstable range, may develop into branches.

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