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Magnetic fields could be a helpful tool for improving the growth of nanostructures on metal layers during electrodeposition processes. It is well known that an electrode-normal magnetic field promotes the growth of mm-sized conical structures by generating a supportive local electrolyte flow. However, we found recently that for smaller cones of μm/nm-size, this local flow may often be superseded by a stronger global cell flow, thus preventing the structuring effect. We therefore discuss improved cell setups to minimize the global flow and to enable the magnetic support of conical growth.

Introduction   Micro- and nano-structured ferromagnetic layers are attractive for numerous applications due to their superior electrocatalytic, superhydrophobic and magnetic properties [1-3]. Among the various methods of synthesizing such structured metal layers, template-free electrodeposition technique appears a cheap and easy method, which usually relies on the use of capping agents in the electrolyte to obtain the desired surface structures [4-6]. However, capping agents could cause undesired changes of the electrolyte properties and also environmental problems. To possibly reduce or avoid the addition of capping agents, we aim to investigate whether magnetic fields could be used to support the local growth of small conical elevations on initially planar electrodes during the electrodeposition of metal. If an external magnetic field is oriented perpendicular to a ferromagnetic electrode surface, magnetic forces will act on the electrolyte. These generate a local flow near conical elevations, which beside a circumferential component is directed towards the tips. The latter could enhance mass transfer of the metal ions, thus supporting conical growth. In more detail, the local flow is driven by the Lorentz force $\boldsymbol{f_L}$ and the magnetic gradient force $\boldsymbol{f_{\nabla B}}$, also known as the Kelvin force [7]:

$$\boldsymbol{f_L} = \boldsymbol{j} \times \boldsymbol{B}, \tag{1}$$

$$\boldsymbol{f_{\nabla B}} = \frac{\chi_{sol}}{\mu_0}(\boldsymbol{B} \cdot \boldsymbol{\nabla})\boldsymbol{B}, \qquad \chi_{sol} = \chi_{H_2O} + \sum_i \chi_i^{mol} c_i. \tag{2}$$

In the Lorentz force density, $\boldsymbol{j}$ and $\boldsymbol{B}$ denote the galvanic current density during electrodeposition and the magnetic flux density applied externally. Induced parts of both quantities can usually be neglected. In the magnetic gradient force, μ_0 and χ_{sol} denote the vacuum permeability and the molar magnetic susceptibility of the electrolyte solution. For aqueous electrolytes at moderate molarity considered here, the latter is built up of the bulk contribution of the diamagnetic water molecules and the local concentration-dependent contribution of the different species in solution that carry magnetic moments [8, 9].

The basic mechanism of locally forcing a downward flow above a surface elevation by an electrode-normal magnetic field was already validated for mm-sized cones [2]. Despite it can be expected that similar local flow pattern are also forced at smaller cones, it is not yet clear whether this flow is still strong enough to significantly enhance the mass transfer. At smaller cones, the flow is forced closer to the surface, and higher wall friction may damp the local flow. Although in the literature this so-called Micro-MHD flow effect has been made responsible for a variety of effects at small scales (see e.g. [10]), measurements of such flows and quantitative estimations of their impact on the mass transfer are still lacking. To get deeper insight into the magnitude of the micro-MHD effect at μm and nm scales, we recently investigated how the local flow and

mass transfer scale with a decreasing cone size, d_{cone} [11]. The scaling laws of the flow velocity, U, caused by the Lorentz, magnetic gradient and buoyancy forces can be summarized as $U_L \sim d_{cone}^2$, $U_{\nabla B} \sim d_{cone}^2$, $U_g \sim d_{cone}^3$, which were obtained by numerical simulations and also confirmed by analytical reasoning. Furthermore, the non-uniform conical growth was found to be limited by the small changes of the metal ion concentration inside the flow region in case of small cones. In order to improve the local mass transfer for micro- and nano-cones, a pulsed current combined with a high magnetic field is recommended [11].

In addition to the local flow near each cone, often also a global flow in the electrochemical cell exists, which might be driven by e.g. solutal buoyancy or magnetic forces acting at the cell scale. This global flow often strongly depends on the size and the orientation of the electrodes. Obviously, this global flow will superimpose the local flow and thus also influence the local mass transfer at the cones.

In a previous work [11], we performed electrodeposition experiments in the electrochemical cell sketched in Fig. 1(a) to obtain of nano-conically structured Ni layers. However, we could not observe enhanced conical growth when a magnetic field is applied perpendicular to the working electrode. By separately simulating both the global and local flow and quantitatively compare their magnitudes near the conical elevations, we were able to interpret the surface morphology of the deposited Ni layers obtained in the experiments. Although the magnetic gradient force generated a beneficial local flow that accelerated the local mass transfer under the applied experimental conditions, this local MHD effect was found to be superseded by the much stronger global flow. This originates from a global Lorentz force caused by the electrode edge effect, and tends to increase the concentration of the metal ions on the electrode, making the deposit layer smoother.

The present work aims to enhance the magnetic structuring effect during the growth of Ni nano-cones by modifying the electrochemical cell to suppress the detrimental global flow. Compared to the original setup with the vertical electrodes introduced in [11], cf. Fig. 1(a), we propose two modified setups with horizontal electrodes (Fig. 1(b-c)) to avoid the vertical shear flow along the cathode caused by buoyancy. Furthermore, we apply the concept of a recessed electrode and install a teflon ring around the working electrode disk. This should reduce the global Lorentz force originating from the deflected current density lines near the edge of the electrode in a vertical magnetic field. In the following, the experimental method and the three cell designs are presented. Further, the numerical method applied is described, followed by a brief analysis of the results obtained for the original vertical electrode setup. After that, the electrolyte flow and mass transfer of the two optimized setups are compared with the original setup, which are then discussed in regard to the surface morphology of the deposited layers in the experiments.

1. Methods   The electrochemical cells considered in this work are sketched in Fig. 1. Here, Fig. 1(a) shows the original setup considered in [11]. The working electrode (WE, $\varnothing$1.9 cm, Cu substrate) and the counter electrode (CE, $\varnothing$5.3 cm, Ni foil) are immersed into the electrolyte and are oriented vertically. An electromagnet (LakeShore EM-4V) is used to provide a uniform magnetic field of 500 mT (uniformity $\pm 0.15\%$ over 1 cm^3 [12]) that is directed perpendicular to the WE surface. As indicated by the red arrows, the current density vectors strongly bend at the edge of the WE. In order to reduce the global buoyancy and Lorentz forces, we introduce a modified setup, Fig. 1(b), where the WE is oriented horizontally. A cylindrical Teflon block ($\varnothing$3 cm, height 2.7 cm) is used to house the electrode and the connection to the power. The CE is a Pt cone-like structure, the bottom of which has the same size and vertically aligns with the WE. A permanent magnet is fixed below the electrochemical cell, vertically aligned with the center of the WE. It generates a surface-perpendicular and quasi-homogeneous magnetic field of 160 mT near the electrode surface. As can be seen, there is still slight bending of the current density lines near the CE and the edge of the WE. We thus further introduce Fig. 1(c), where a teflon ring is installed around the WE. This ensures that the current density lines enter the WE vertically. Deflected current density vectors are observed only near the CE and at the upper part of the teflon ring. If not otherwise stated, the electrolyte consists of 200 g/l NiCl$_2$·6H$_2$O, 100 g/l H$_3$BO$_3$ and 10 g/L NH$_4$Cl as a capping agent in all three cases. After a galvanostatic electrodeposition at 20 mA/cm^2 for 5 min, the surface morphology of the deposited layers, i.e. a Ni film covered by Ni nano-cones, is analysed.

Based on the configurations sketched in Fig.1, numerical simulations are performed to calculate the global cell flow for each setup, where the WE is assumed to be a planar surface. Additionally, we simulate the local flow driven by the magnetic forces near a Ni cone by applying periodic boundary conditions. This
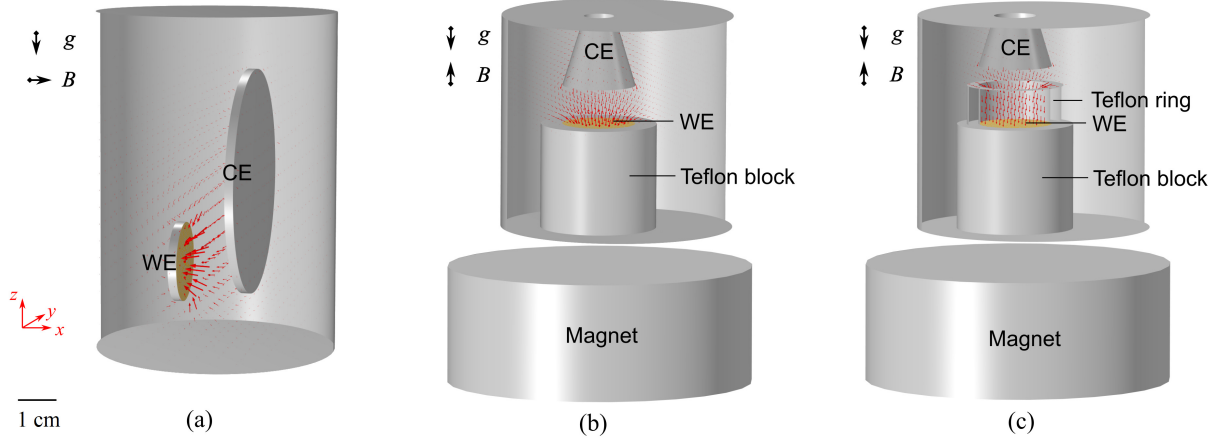
Figure 1: Sketch of the electrochemical cell of (a) the original setup considered in [11], (b) the modified setup without a teflon ring, and (c) the modified setup with a teflon ring installed around the WE. Red arrows represent the current density vectors.

two-step approach is necessary to properly resolve the flow at different length scales and to give quantitative information on the relation between global and local flow effects, which will be used for discussing the deposition results obtained experimentally. More details of the numerical model are given in [11].

2. Results

2.1. Vertical electrode setup (a)   In general, an electrode-normal magnetic field causes a Lorentz force f_L which gives rise to a primary azimuthal flow around each cone. Then, due to centrifugal acceleration, a secondary electrode-normal flow towards the cones appears. For ferromagnetic layers such as Fe, Ni, additionally a magnetic gradient force $f_{\nabla B}$ is present, which is also generating a downward flow towards the cone tips. Thus, both magnetic forces are supporting conical growth [7]. Although these local flows become weaker with decreasing cone size, a supportive local flow at nm-sized ferromagnetic cones is expected. However, applying a strong perpendicular magnetic field has not yet led to improved conical growth in the deposition experiments performed so far [11].

To understand this phenomenon, we now present simulation results of the deposition experiments that beside the local flow near the cones include also the global cell flow. As shown in Fig. 2 (Left), near the circular WE that is smaller than the CE (see Fig. 1(a)), a circumferential primary flow is driven by the Lorentz force that arises from the deflection of the current density vectors near the electrode edge of the WE, thereby also causing an electrode-normal secondary flow. Additionally, Fig. 2 (right) shows the supportive local flow near a cone that for small cones is dominated by the action of the magnetic gradient force. Bringing both flows in a quantitative comparison, we find that the magnitude of the global flow velocity near the cone surface is about 13 times larger than that of the local flow. In other words, the local flow and its support for conical growth becomes superseded by the much stronger global flow, which tends to enhance the overall surface concentration and to reduce the surface roughness.

2.2. Optimized electrode setups (b-c)   In order to reduce the global flow, we propose two modified configurations of the electrochemical cell as sketched in Fig. 1. The streamlines of the global flow velocity of different cell setups are compared in Fig. 3. In the original setup (a), as mentioned above, strong primary and secondary flows are driven by the global Lorentz force. In the modified setup without a Tefon ring (b), the bending of the current density lines near the CE and the edge of the WE also causes rotational primary flow, which is however lower in magnitude compared to that of the original setup. If a teflon ring is additionally installed (c), the global MHD flow originates only from the deflected current lines near the
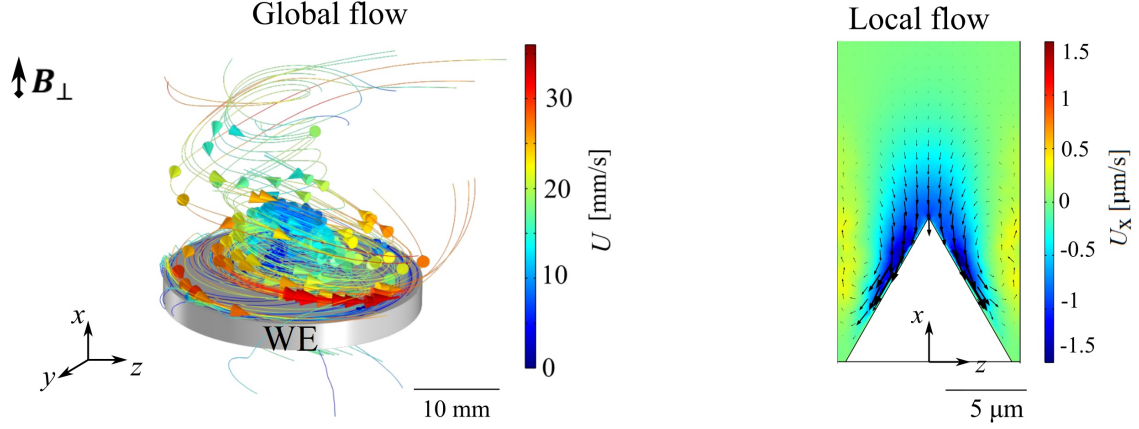
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Figure 2: Numerical results of the global flow near the WE (left) and the local flow velocity in a vertical plane passing the cone center (right) after a steady-state is reached. For better visibility, the WE is shown in horizontal orientation, compared to Fig. 1(a). Please further note the different magnitudes of the global and the local velocity. Adjusted from [11].

CE and the upper part of the teflon ring. Although it could not be completely eliminated, its magnitude is further reduced compared to the case without a teflon ring.
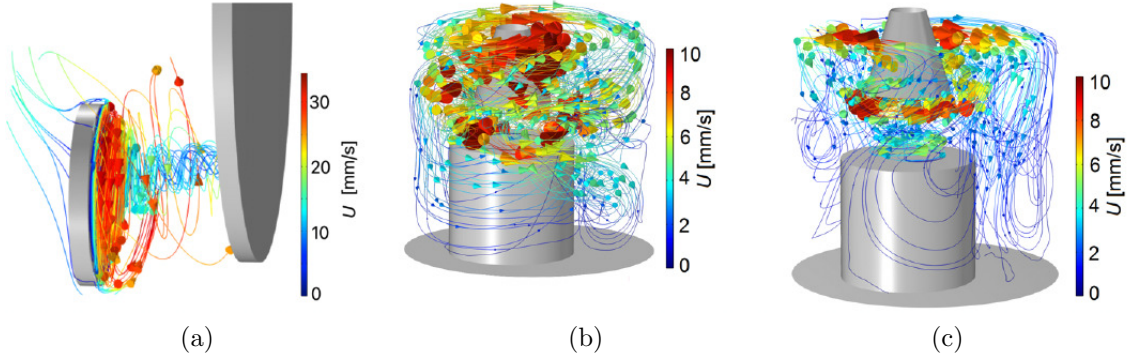

Figure 3: Numerical results of the 3D streamlines of global flow at 60 s. (a) Original setup; (b) Modified setup without teflon ring; (c) Modified setup with teflon ring.

Fig. 4 quantitatively compares the magnitudes of the flow velocity on a vertical plane passing the center of the WE. In line with the results presented in Fig. 3, the global flow is effectively reduced in the two modified setups. If a teflon ring is used, the edge effect of the WE could be avoided (see Fig. 1(c)). But the primary flow originating from the upper part of the teflon ring still generates a secondary flow which eventually also reaches the WE.

Comparing the flow velocity in the vicinity of the center of the WE surface, Fig. 5, we notice that for the two modified setups the magnitude of the flow velocity at a distance of 2 μm to the surface ($\sim$ height of nano-cones) is similar and much weaker than for the original setup. To investigate the influence of the global flow on the mass transfer, we analyze in Fig. 5b the temporal development of the concentration of Ni^{2+} ions averaged over the whole WE, $c_{Ni^{2+},avg}$. Without electrolyte convection, $c_{Ni^{2+},avg}$ should decrease in time during the deposition, scaling with $\sqrt{t}$ [13]. However, a decrease of $c_{Ni^{2+},avg}$ is observed only in the first $10 - 30$ seconds of all cases considered here, indicating the development of a global flow which brings bulk electrolyte towards the WE and compensates for the consumption of the metal ions there. This enables a steady-state concentration to be reached after a certain period of time. The highest surface concentration is observed in the original setup, followed by the modified setup without and with a teflon
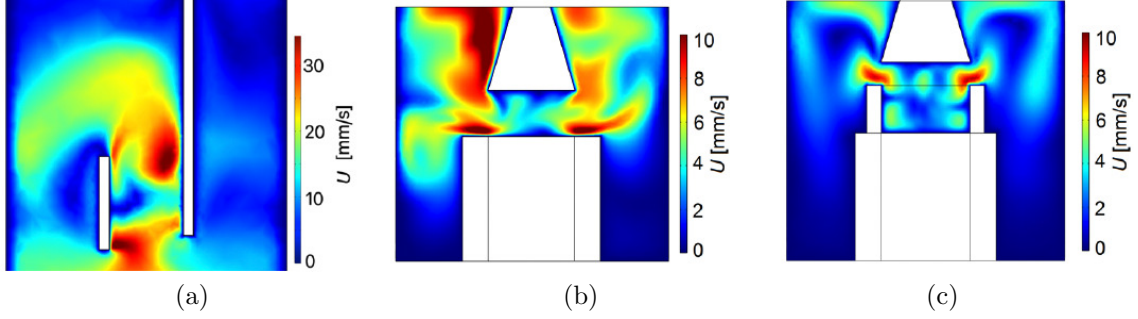
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(a)   (b)   (c)

Figure 4: Numerical results of the velocity magnitude in the vertical planes passing through the center of the anode and cathode at 60 s. (a) Original setup; (b) Modified setup without teflon ring; (c) Modified setup with teflon ring. Please note the different velocity scales. The asymmetry of the flow velocity visible in (b) is due to the slight asymmetry in the cell geometry, see Fig. 1(b).

ring, which corresponds to the different magnitudes of the global flow velocity shown in Fig. 4. Specially, if the electrodes are oriented vertically (Fig. 1(a)) but no magnetic field is applied, a global buoyancy flow stabilizes the surface concentration as well. This shows the significance of a horizontal arrangement of the electrodes to reduce the unfavorable global buoyancy effect.

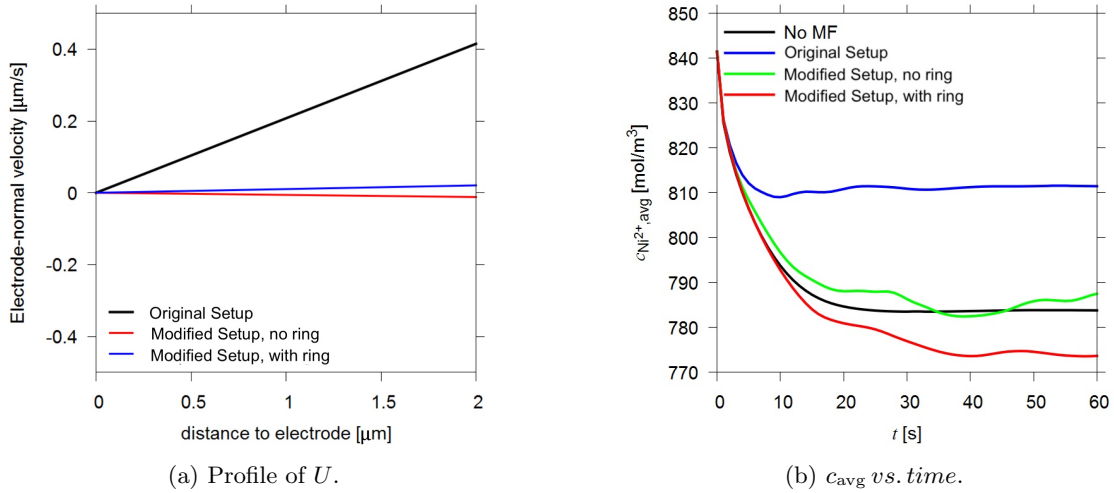(a) Profile of U.   (b) $c_{\mathrm{avg}}\, vs.\, time$.

Figure 5: (a) Velocity profile along a line passing the center of the electrode and perpendicular to the electrode surface. (b) Temporal evolution of the concentration of Ni^{2+} ions averaged over the whole WE for different setups. "No MF" denotes the case of the Original setup without magnetic field.

Table 1: Roughness (nm) for different amounts of NH$_4$Cl and different cell setups measured by AFM.

NH$_4$Cl	Original setup	Modified setup, no ring	Modified setup, with ring
0 g/L	116.30	102.82	113.95
5 g/L	104.80	121.53	154.00
10 g/L	104.73	125.00	145.00

Although the global flow could not completely be avoided in the modified setups, we remark that its magnitude compared to the local flow is significantly reduced. According to the simulation results, the ratio of the maximal global flow and local flow velocities decreases from 13 (Fig. 2) of the original setup to 5 of

the modified setups, suggesting that the local support for the conical growth could be enhanced. In order to confirm this, AFM analyses are performed for the deposit layers obtained in the experiments. As can be observed in Fig. 6, the width and height of the cones are larger in the modified setups compared to the original one. The elongation of some of the structures in (c) is suspected to be visualization artefacts in the AFM analyses. Table 1 further lists the surface roughness computed from the AFM results. Except for the case without capping agent (0 g/L NH_4Cl), the roughness in general is largest in the case with a teflon ring, followed by the modified setup without a ring. This indicates an improved conical growth and enhanced magnetic structuring effect when the global cell flow is reduced.
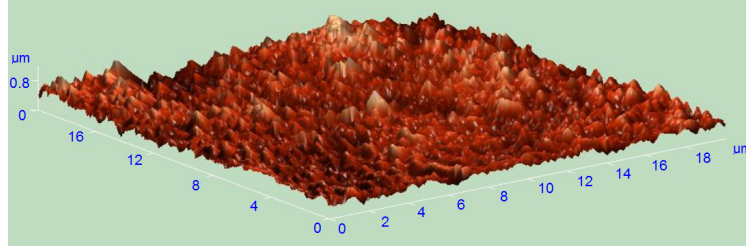
(a) Original setup
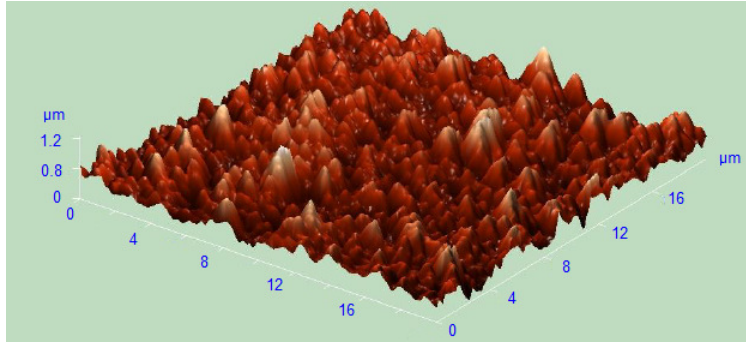
(b) Modified setup, no ring
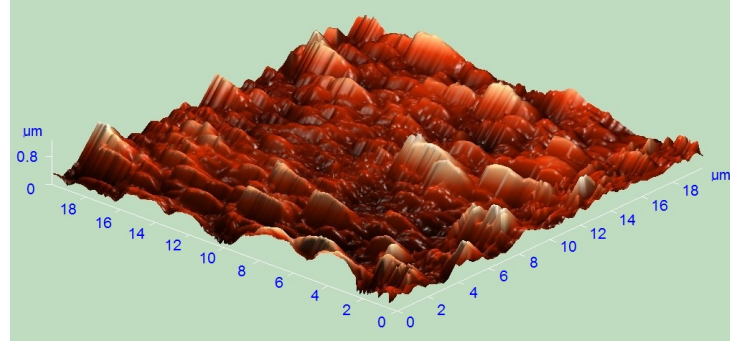
(c) Modified setup, with ring

Figure 6: AFM analysis of the deposit layer of different setups, 10 g/L NH_4Cl added. Please notice that the vertical scaling differs in the subfigures.

3. Conclusions During the electrodeposition of nano-structured ferromagnetic layers in electrode-normal magnetic fields, the magnetic gradient force drives a beneficial local flow that supports conical growth. However, this supporting effect is much weaker compared to that at larger, e.g. mm-sized cones. It can therefore easily be superseded by a global cell flow that may be caused by the edge effect of electrodes due to the Lorentz force. In order to minimize the detrimental global flow, we performed deposition experiments

in carefully designed electrochemical cells. A horizontal electrode arrangement was used to avoid electrode-parallel buoyant flow, and equally sized electrodes and/or a recessed WE were used to ensure nearly parallel electric field lines. Numerical simulations show that these measures effectively reduce the global flow near the WE surface when compared to the original cell design. AFM analysis of the metal layers deposited in the experiments shows that a higher surface roughness is obtained in the optimized cells, indicating that the magnetic support for conical growth was enhanced. Future efforts in cell design may continue to reduce the global cell flow to further strengthen the structuring effect in magnetic fields.

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