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TITLE:

Localized Bathless Metal-Composite Plating via Electrostamping

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SUMMARY:

Presented here is a protocol of bathless electroplating, where a stagnant metal salt paste containing composite particles are reduced to form metal composites at high loading. This method addresses the challenges faced by other common forms of electroplating (jet, brush, bath) of embedding composites particles into the metal matrix.

ABSTRACT:

Composite plating with particles embedded into the metal matrix can enhance the properties of the metal coating to make it more or less conductive, hard, durable, lubricated or fluorescent. However, it is more challenging than metal plating, because the composite particles are either 1) not charged so they do not have a strong electrostatic attraction to the cathode, 2) are hygroscopic and are blocked by a hydration shell, or 3) too large to remain stagnate at the cathode while stirring. Here, we describe the details of a bathless plating method that involves anode and cathode nickel plates sandwiching an aqueous concentrated electrolyte paste containing large hygroscopic phosphorescent particles and a hydrophilic membrane. After applying a potential, the nickel metal is deposited around the stagnant phosphor particles, trapping them in the film. The composite coatings are characterized by optical microscopy for film roughness, thickness and composite surface loading. In addition, fluorescence spectroscopy can be used to quantify the illumination brightness of these films to assess the effects of various current densities, coating duration and phosphor loading.

INTRODUCTION:

Traditional electroplating is widely used to deposit thin films of a variety of metals, alloys, and metal-composites onto conductive surfaces to functionalize them for the intended application[1-12]. This method adds a metal finish to parts used in the manufacturing of aerospace, automotive, military, medical, and electronic equipment. The object to be plated, the cathode, is submerged in an aqueous bath containing metal salt precursors, which are reduced to metal at the surface of the object by the application of a chemical or electrical potential. Non-charged composite particles can be incorporated into the metal film by adding these to the bath during coating to enhance the film properties for increased hardness in the case of metal oxides and carbides, smoothness with polymers or lubrication with liquid oils[12,13]. However, because these particles lack an inherent attraction to the cathode, the ratio of composite that is incorporated into the metal remains low for bath plating[13-15]. This is especially problematic for large particles that do not adsorb to the cathode long enough to be embedded by the growing metal film. Additionally, hygroscopic particles solvate in aqueous solutions and their hydration shell acts as a physical barrier impeding contact with the cathode[16].

Some promising methods have been shown to mitigate this effect by using dry non-polar solvents to remove the hydration barrier completely[17], or by decorating the composite particles with charged surfactant molecules[16] that disrupt the hydration shell to allow contact between the particle and the cathode. However, because these methods involve organic materials, carbon contamination is possible in the film and breakdown of these organic materials could occur at the electrodes. For example, the organic solvents used ($DMSO_2$ and acetamide) are heated to 130 °C in an inert atmosphere for air-free coating; however, we found them to be unstable during coating in air. Due to resistive heating at the electrodes, redox reactions with organic materials may result in impurities or sites for heterogeneous nucleation and growth of metal nanoparticles[18]. As a result, there is a need for an organic-free aqueous electroplating method that addresses the long-standing challenge of particle-cathode adsorption. So far, metal-composite bath coating has been shown to embed particles up to a few micrometers in diameter[19] and as high as 15 % loading[16,17].

In response to this, we describe an inorganic bathless electrostamping method that forces composite particles to become embedded into the film at high surface coverages despite their large size and hygroscopic nature[20]. By removing the bath, the process does not involve containers of hazardous coating liquids and the object to be plated does not need to be submerged. Therefore, large, cumbersome or otherwise corrosion- or water-sensitive objects, can be plated or “stamped” in select areas with the composite material. In addition, the removal of excess water requires less clean-up of liquid hazardous waste.

Here, we demonstrate this method to produce bright fluorescent metal films by co-depositing non-toxic and air-stable europium and dysprosium doped, strontium aluminate (87 ± 30 µm) with nickel at high loadings (up to 80%). This comes in contrast to previous examples that were plated in a bath and therefore were limited to small (nanometers to a few micrometers) phosphors[12]. In addition, previously reported electrodeposited films fluoresce only under short-wave UV-light, with the exception of a recent report that grew 1 – 5 µm luminescent strontium aluminate crystals in an alumina film with plasma electrolyte oxidation[21]. Fluorescent metal films could have far-reaching applications in many industries involving dim-light environments including road sign illumination[21], aircraft maintenance equipment location and identification[20], automobile and toy decorations, invisible messages, product authentication[22], safety lighting, mechanochromic stress identification[10] and tribological wear visual inspection[12,16]. Despite these potential uses for glowing metal surfaces, this method could also be expanded to include additional large and/or hygroscopic composite particles to produce a new variety of metal-composite functional coatings that were previously not possible via electroplating.

PROTOCOL:

1. Preparing coating salts

CAUTION: Nickel salts and boric acid are toxic and should be handled with proper personal protective equipment including nitrile gloves, goggles and a lab coat. Strong acids and bases should be handled in the fume hood, and all waste chemicals should be disposed of as hazardous waste.

1.1 Using a balance, weigh out the following powders in these ratios: 10.000 g of $NiSO_4 \cdot 6H_2O$, 2.120 g of $NiCl_2 \cdot 6H_2O$, 1.600 g of H_3BO_3 and combine in a vial together. See **Table 1** for concentrations.

1.2 Weigh out 1.800 g of $SrAl_2O_4:Eu^{2+}$, Dy^{3+} phosphor or alternative phosphors including europium doped yttrium oxide, europium doped barium magnesium aluminate, or replace with alternative oxide, metal, or organic composite material depending on the desired effect.

NOTE: The amount added here may vary based on the properties of the composite material and the desired qualities of the metal-composite film.

1.3 Using a porcelain mortar and pestle, grind the composite powder for approximately 10 minutes until it becomes a fine powder.

NOTE: This does not change the particle size, but does separate aggregated particles.

1.4 Likewise, grind the salt mixture from step 1.1 in batches until it becomes a fine powder.

1.5 Combine the ground phosphor with the ground salt mixture in a container for storage.

1.6 Weigh out 0.188 grams of the mixture per cm^2 of coating area, as prepared in step 1.5 and add to a container with an open top that is easy to access.

1.7 To this, add 40 µL of water per cm^2 of coating area, and stir to partially dissolve the salts forming a thick paste. Set this aside.

NOTE: The protocol can be paused here.

2. Preparing the electrodes

2.1 Using scissors, cut the anode to the size and shape that matches the object to be plated. In this example, we prepare a 4 cm^2 nickel foil to be coated, and a 4 cm^2 nickel anode is cut to match this.

NOTE: Other objects can be coated including large objects. In this case, select the area on the object to be coated, and cut out the anode to match the coating area.

2.2 Using a cotton swab or a cloth, clean the surface of the anode foil and the cathode (coating object surface) with concentrated (10 M) potassium hydroxide or sodium hydroxide base to remove organic material. Next, rinse the surfaces with water to remove excess base.

2.3 Using a cotton swab or a cloth, activate the object surface with concentrated acid. In the case of nickel, 37% vol/vol HCl is used, although for steel, 10% by volume aqueous HCl may be more appropriate. Please refer to the recommendations for activating metal surfaces provided elsewhere to determine the appropriate method for activating specific metals or alloys[23,24].

NOTE: After this step, the metal surface is reactive and the surface will start to react with oxygen in the air to form an oxide layer. This will cause the surface to be inactive, so the following steps (2.4 – 3.5) should be performed in the next 5 minutes; otherwise, step 2.3 should be repeated before continuing.

CAUTION: This step should be performed in a fume hood to avoid exposure to HCl vapors.

2.4 Quickly, deposit the coating paste onto the cathode object. In this case, the cathode is a 4 cm^2 nickel foil on the benchtop. Cover the object area to be plated evenly and try to avoid gaps in the paste.

NOTE: In this example, we are painting on this paste with two scoopulas, however, other options may include spraying, dipping or doctor blading to increase the speed and efficiency of this step.

2.5 Using a cotton swab or a cloth, activate the anode with concentrated acid by dipping the swab in the acid and gently rubbing the cathode surface. In the case of nickel, 70% vol/vol HNO_3 can be used.

NOTE: However, other acids may be more appropriate for specific metals and alloys. Please refer to the recommendations provided elsewhere for the appropriate reagent to activate specific anode surfaces[23,24].

CAUTION: This step should be performed in a fume hood to avoid exposure to NO_2, a toxic brown gas that is formed during the reaction. Continue treating the surface until the surface becomes grey and textured. After this step, the metal surface is reactive and the surface will start to react with oxygen in the air to form an oxide layer, so the following steps should be performed quickly to avoid inactivation of the anode.

2.6 If calculating the current efficiency is desired, use an analytical balance to record the mass of the anode and the cathode.

3. Assembly and coating

3.1. Pre-set a power supply to the desired current in constant current mode or voltage, if constant voltage mode is desired. In this example, constant current mode is used with a current of 0.1 Amperes (0.1 A per 4 cm^2 = 0.025 A/cm^2).

NOTE: For larger or irregularly shaped objects, the coating area can be predetermined with a grid or using a photo with scale bar and an imaging software like ImageJ. The applied current can be scaled to deliver the same current density required for the coating area.

3.2. Cut a piece of nylon sheet (or alternative hydrophilic membrane) to a size larger than the anode so that the anode does not make direct contact with the cathode object.

3.2.1 Place the nylon sheet on top of the coating paste, and then add a small amount of paste to this.

3.3. Next, add 1-2 drops of water from a pipette to allow the salt to partially dissolve. Steps 3.2.1 – 3.3 make the nylon sheet conductive and allow for the mass transport of ions through the electrolyte, which is necessary to balance charge in the coating reaction.

3.4. Finally, add the activated anode on top and attach the negative lead to the cathode object and the positive lead to the anode.

NOTE: It might be helpful to tape down these leads so that the setup remains stationary, especially if the experiment involves small pieces of metal foil. This is less important for large objects.

3.5. Cover the system with plastic or seal to help retain water, and apply moderate pressure (~100 g per cm^2 area), turn on the power supply and continue coating for the desired duration.

3.6. Turn off the power supply and expose the system.

3.7. Disconnect the leads, separate the electrodes and rinse the cathode object with water into a waste container.

3.7.1. Soak the other items in water to remove salts and dispose of this aqueous solution in the properly labeled hazardous waste container

3.7.2. Wearing gloves, gently rub the cathode object by hand to remove any uncoated composite particles. The coating is complete and ready for characterization.

3.7.3. Using an analytical balance, record the mass of the anode and the cathode and find the difference between these values and their original mass.

3.7.4 Use Faraday's Laws of electrolysis to calculate the current efficiency. The theoretical moles of metal coating can be determined using Equation 1.

$$n = \frac{It}{Fz} \qquad \text{Equation 1}$$

where n is the amount of metal deposited (units: mol), I is the applied current, t is the coating time, F is Faraday's constant (96485 coulombs per mole) and z is the charge of the metal ion. Calculate this value based on the experimental parameters.

3.7.5 Divide the experimentally determined deposit mass obtained from the masses of the cathode or anode (Steps 2.6 and 3.7.3) by the theoretical mass lost (anode) or gained (cathode) to calculate the current efficiency using Equation 2.

$$Current\ Efficiency\ (\%) = \frac{experimental\ deposit\ mass}{theoretical\ deposit\ mass} x\ 100 \text{ Equation 2}$$

[NOTE: At a current efficiency of 100%, under constant voltage, a theoretical deposit mass is expected of approximately 1.095 g of nickel or 12.3 µm of nickel per hour, given 0.04 A and 4 cm^2 area. Likewise, under constant current, approximately 614.6 µm nickel would theoretically deposit per unit of 1 $A \cdot cm^{-2}$ after 30 min.]

4. Characterization with electrochemistry

4.1. Use chronopotentiometry to monitor changes in voltage under constant current, and chronoamperometry to monitor changes in current under constant voltage.

4.1.1. Turn on the potentiostat and designate the duration and the applied current or voltage.

4.1.2. Repeat steps 3.2 – 3.5 to prepare the coating.

4.1.3. Use a calibrated 3-electrode system to normalize the voltage to a reference standard.

4.1.3.1. Place a platinum wire pseudo reference electrode between on top of the nylon sheet and below the anode. In order to ensure that the reference electrode does not make direct contact with the anode, use a separate nylon sheet (or alternative membrane) placed on top of the reference followed by a few drops of water, a small amount of coating paste (repeat steps 3.2 –

3.3) and then the anode.

4.1.4. Connect the leads to the electrodes, seal, press, begin coating and monitor changes in voltage or current.

5. Characterization with quantum yield fluorescence spectroscopy

5.1. If the coating contains fluorescent composite particles, use a fluorometer equipped with an integrating sphere to obtain absolute quantum yield measurements.

5.1.1. Place the coating into the fluorimeter stage with the fluorescent coating facing 45° from the excitation source and 315° from the detector.

5.1.2. Record the fluorescence spectra starting at a wavelength below the excitation wavelength to record the areas of the excitation peak and the fluorescence peak.

5.1.3 Remove the sample from the fluorometer, and repeat step 5.1.2 to record the blank excitation peak. Calculate the quantum yield (QY) from the ratios of the areas of the excitation and emission peaks (Equation 3 and **Figure 3B**).

$$QY(\%) = \frac{A_{em}}{A_0 - A_{ex}} \times 100 \quad \text{Equation 3}$$

where A_{em}, A_{ex} and A_o are the peak areas at the emission wavelength of the sample, the excitation wavelength of the sample and the excitation wavelength of the blank, respectively.

6. Characterization with optical microscopy

6.1. Place the sample on the stage of a calibrated optical microscope with the coating side facing the lenses and bring the surface into focus.

6.2 Record surface images at the desired magnifications and surface sample sites.

6.3 Using image analysis software (ex. ImageJ (IJ 1.46r)), calculate and plot the surface coverage and average composite particle size.

6.4 To determine coating thickness and cross-section features, cut the cathode foil with scissors. Set the coating on the side and re-adjust the focus. Repeat steps 6.2 – 6.3.

REPRESENTATIVE RESULTS:

After following this protocol, a thin coating of metal should become plated onto the cathode surface and contain the composite particles that were added to the coating paste. Fluorescent or colored particle incorporation can be observed by visual inspection as a result of a change in appearance compared to the uncoated surface (**Figure 1A1-A3**). To investigate the percent surface coverage of the composite particles and to observe the surface morphology of the coating, optical microscopy can be used (**Figure 1**). Samples can be observed top-down (**Figure 1B1-B3** and **1C1-C3**) or cut to reveal the cross-section (**Figure 1D1-D3**). This works for observing microscale composite particles and microscale features in the metal coating. However, nanoscale composite particles and nanoscale morphological features should be observed with a scanning electron microscope[19,25-27]. Imaging software can be used to calculate the sizes and surface coverage of the composite particles by including data from images of several areas over the coated surface.

The results of this analysis can be plotted to show the effects of applied current and/or coating duration on the amount of particle loading (**Figure 2A**). In general, particle surface coverage increases with time and with current density. For coatings under constant voltage, the surface coverage increases steadily up to 80% after 18 h at a rate of 0.066% per min. For constant current deposition, the particle surface coverage increases rapidly at low currents and then levels off at current densities above 0.025 A·cm^{-2}. The reason for this is likely due to the observation that coatings at 0.25 A·cm^{-2} were rough (**Figure 1A1**) and a nonuniform coating corresponded to a runaway voltage due to increased resistance (**Figure 2A**). Therefore, an optimized current density was identified at 0.025 A·cm^{-2} for nickel and strontium aluminate phosphor particles, but this parameter may need to be re-determined when changing the metal salt or the composite material.

The thickness of the films increases with time and current density as well, and interestingly the surface coverage is also correlated with thickness (**Figure 2B**). This is expected because as the film thickness increases, it has the capacity to contain more particles. Coating parameters like these can be monitored by electrochemistry under constant current with chronopotentiometry and under constant voltage with chronoamperometry (**Figure 3A**). Under constant voltage, the resistance increases steadily and, as a result of Ohm's law, the current density decreases. Fluctuations in the current can be explained by periodic plating of layers rich in composite particles (high resistance) alternating with layers of metal atoms (low resistance). Under constant current, the resistance stays steady for about 30 minutes; however, at some point, the resistance increases rapidly and the coating becomes unstable. This can be observed in the optical microscope (**Figure 1A1**) where high currents can lead to inconsistent and rough coatings. Likewise, low currents also produce inconsistent coatings with low composite loading as a result of the low driving force to deposit (**Figure 1A3**). In contrast, optimized current densities are required for uniform coatings (**Figure 1A2**). Under optimized conditions, the current efficiencies remain high (85-95%) as calculated from Equations 1 and 2. However, at either high current densities (> 0.025 A·cm^{-2}) or long durations (> 1 h), we observed a decrease in coating efficiency as the particle loading increases. For example, the film thickness of this metal composite does not increase as would be expected for pure nickel despite higher applied currents (**Figure 1D1-D3**).

For fluorescent or phosphorescent metal-composite coatings, fluorescence spectroscopy can be used to quantify the brightness and the luminescence quantum yield (**Figure 3B**). An integrating sphere encloses the sample in a reflective dome and allows light to travel through two openings separated by 90°. The excitation light that travels to the blank sample (no coating) will have minimal absorbance and maximum reflection. Light reflects off of the sample, scatters around the integrating sphere and escapes through the opening behind the sample. The coating surface is angled at 45° from the excitation light and 315° from the detector. When the spectrum is repeated with a fluorescent sample, the excitation peak diminishes as a result of absorbance, and the emission peak appears. The shape of the emission peak(s) and the wavelength is recorded. In addition, the ratios of the peaks can be used to calculate the luminescence quantum yield following the equation given in **Figure 3B**. In general, the phosphorescence brightness of the film increases linearly with particle surface loading (**Figure 1A1-A3**), which is controlled by film thickness (**Figure 2B**). The quantum yield was found to correlate proportionally to the particle surface coverage by Gerwitz et al., and this reference includes more discussion on this topic[20].

FIGURE/TABLE LEGENDS:

Table 1. Recipes for Traditional Bath Plating and Electrostamping. These are based on Watts's nickel bath plating solution and corresponding electrostamping methods where the relative amounts of dry reagents are the same for each. However, the amount of added water is significantly different which increases the concentrations (g/L solution). Also included are typical current densities ($A \cdot cm^{-2}$), possible composite particle sizes (µm) and loading amounts (%).

Figure 1. Representative images of composite coatings. This includes photos of 4 cm^2 films in the dark 5 seconds after excitation with visible light > 400 nm was removed (**A**), top-view optical microscope images in the dark under an FTIC filter and continuous 470 ± 20 nm excitation (**B**), and under brightfield light conditions (**C**), including cross-section images (**D**), after coating for 30 minutes with applied current of 1.0 A (0.25 $A \cdot cm^{-2}$) (1), 0.1 A (0.025 $A \cdot cm^{-2}$) (2), and 0.01 A (2.5×10^{-3} $A \cdot cm^{-2}$) (3). This figure has been modified from Gerwitz et al.[20]

Figure 2. Representative analysis of microscopy images. This includes the composite surface coverage (%) as a function of time for chronoamperometry (blue) and as a function of current density ($A \cdot cm^{-2}$) for chronopotentiometry (red) during coating of a 4 cm^2 nickel foil sample after 30 min (**A**). Additionally, the surface coverage can be plotted with the film thickness as measured from the cross-section (**B**). This figure has been modified from Gerwitz et al.[20]

Figure 3. Representative electrochemical analysis during the coating process and fluorescence quantum yield measurements. This includes chronoamperometry (blue) and chronopotentiometry (red) during coating of a 4 cm^2 nickel foil sample over time (**A**). Solid state stage fluorescence spectra of a 4 cm^2 nickel foil sample coated for 30 min at 0.025 $A \cdot cm^{-2}$ under constant current, plotted with the spectra from the blank metal film (**B**). The ratios of the peak areas are used to calculate photoluminescence quantum yield using the equation provided where A_{em}, A_{ex} and A_o are the peak areas at the emission wavelength of the sample, the excitation wavelength of the sample and the excitation wavelength of the blank, respectively. This figure has been modified from Gerwitz et al.[20]

DISCUSSION:

Critical steps of electrostamping. Bathless electrostamping shares many of the same critical steps with traditional bath electroplating. These include proper cleaning of the electrodes, mixing metal ions into the electrolyte and applying and external or chemical (electroless plating) potential to cause reduction of metal onto the cathode. In addition, the oxidation of the anode and cathode should be avoided after acid activation by quickly rinsing with water and adding these electrodes to the setup.

Electrostamping compared to traditional bath plating. A few metal-composite fluorescent metal films have been reported from bath plating[16,17,28]. However, in order to overcome the low physisorption of the composite to the cathode, some inventive methods have been demonstrated. These include removing the water and using dry organic solvents[17], decorating the composite particles with charged surfactants to disrupt the hydration shell[16] or only attempting the process with non-hygroscopic particles[22,28,29]. However, these methods continue to be limited to low surface coverages, small particle sizes from nanometers to a few micrometers[12], and the potential for organic material incorporation. In contrast, the electrostamping method introduced in this report traps the composite particles in a stagnant electrolyte paste during coating, which forces the composite particles to remain near the cathode long enough to become embedded into the nickel matrix as it grows around them. **Table 1** compares the recipes of both bath plating and electrostamping and highlights the effect of removing the majority of the water from the solution. For a 4 cm^2 coating, the volume of the paste is approximately 0.5 mL. Without a liquid bath, the coating paste can physically contain the composite particles to allow for larger composites to be coated and also at higher loading amounts. It should be noted that even though the concentrations are expressed in grams per liter of solution, electrostamping does not require a liquid bath.

Interestingly, the power consumption required for plating is also comparable to bath plating. For example, in a typical bath, 0.02 – 0.07 $A \cdot cm^{-2}$ current densities are employed, which is a range that contains the 0.025 $A \cdot cm^{-2}$ current found to be optimal for bathless electrostamping. The resistivity of the electrolyte also plays a role, where lower resistance values lead to lower voltage requirements as a result of Ohm's Law. In bath plating, the electrolyte solution is often heated (80 – 90 °C) to decrease the resistance, which is also a source of power consumption. In contrast, for bathless coating, the concentration of metal salts in the electrolyte is significantly higher (**Table 1**), which leads to a low electrolyte resistance[20] (14-35 Ω for the samples here), even at room temperature. This results in power requirements of 2.0 V, 0.025 $A \cdot cm^{-2}$ and 50 $mW \cdot cm^{-2}$ for electrostamping of the metal-composites (**Figure 3A**). Without the presence of composites, we would expect the power demand to be lower than traditional bath plating as a result of the lower resistivity of the concentrated electrolyte. However, since this method is used to deposit high levels (up to 80%) of uncharged particles in the metal matrix, their presence in the film inherently increases the resistivity of the cathode. This effect may explain the lower than expected thicknesses as the ceramic particles occupy more of the nickel surface, decreasing the available sites for nickel reduction and film growth.

Limitations of electrostamping. A limitation of this method includes the potential for non-uniform coating if the electrolyte paste does not reach the crevices of complex surfaces. Whereas bath electroplating can be used to deposit a uniform coating over the entire surface of an object, electrostamping provides a localized deposition. This may lead to an uneven thickness and roughness distribution. For some applications were dimensions are critical, this method may need additional adjustments (sanding, polishing etc.) after deposition to account for discrepancies in thickness. Additionally, as a result of bringing the plating system out of the bath, surface coverages of up to 80 ± 12% are possible[20], even with large (87 ± 30 µm) hygroscopic composite particles and without organic reagents. However, at high loadings, a compromise must be made between durability and functionality. As the percentage of composite material increases, the film properties begin to deviate away from the original metal matrix toward the properties of the composite material, which is often a brittle powder. As a result, high coverages above 50% may not be practical for many applications that require durable metal films.

Electrostamping compared to localized jet and brush plating. Bath plating can be used to selectively etch/plate specific areas on conductive objects by protecting the rest of the object with masking tape as the cathode is submerged. However, like electrostamping, jet plating and brush plating can deposit metal onto localized areas without a bath. In jet plating, an electrical potential is established between the cathode (object to be coated) and a stream of jetting electrolyte as it passes from the anode nozzle[30]. A plating potential is established through the jet, and the metal salts can be reduced at the surface. Likewise, the surface can also be etched under reversed polarity. This method has applications in electronic fabrication where small deposits can be jet-printed onto a circuit board. Similarly, brush plating also involves a flow of electrolyte out of an anode covered in an absorbent cloth[31]. The anode brush holds the flowing electrolyte and when it contacts the cathode object, the metal salts are reduced at the surface to produce a highly controllable thickness. This method is used for repair of large metal parts and these parts are often spinning during plating to increase the uniformity of the coating.

Both jet and brush plating involve a flowing liquid electrolyte. For this reason, they are amenable to pure and alloy metal plating. However, these methods would not be ideal for composite-metal plating. The challenges facing embedding composite particles into the cathode film in a bath are also present with these methods, especially for large and hygroscopic particles. In order to promote the capture of these particles within the growing metal film, the solution flow should be stagnant. Electrostamping is a new technique that addresses this problem by coating metal and composites with no solution flow. For this reason, electrostamping stands out as a unique method for coating in general, which may become a more commonly accepted method for locally depositing pure metal as well as metal composites.

Troubleshooting electrostamping. Potential troubleshooting of absent or inconsistent coatings can be addressed by checking the following. 1) The metal electrodes may not be cleaned effectively with base so that a hydrophobic organic material barrier prevents plating. 2) The metal electrodes are not effectively activated with acid, or have been exposed to air for more than 5 min so that a less conductive metal oxide layer barrier forms and prevents plating. 3) The paste is not viscous enough and does not trap the composite particles or is too dry and causes a high resistance through the electrolyte.

Future applications of electrostamping. For many objects, electrostamping could be advantageous over traditional bath plating. For example, if the object to be coated is large, cumbersome, delicate or sensitive to corrosion, then a selected area can be “stamped” onto the side of the object. Examples may include the sides of appliances, road signs, metal fences, sides of buildings, covert messages onto walls, laptop computers, metal hand tools, or automobile and aircraft components. In addition to the potential versatility of this method to coat objects that were previously considered not possible, this method opens the door to future investigation of other metal-composite combinations, at higher surface loadings and with larger or hygroscopic particles. Here, we demonstrate this method for metal oxide composite/nickel metal matrix coatings; however, this method may motivate the investigation of multiple different metals and alloys, with a variety of composite particles that have not yet been realized.

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DISCLOSURES:

The authors have nothing to disclose.

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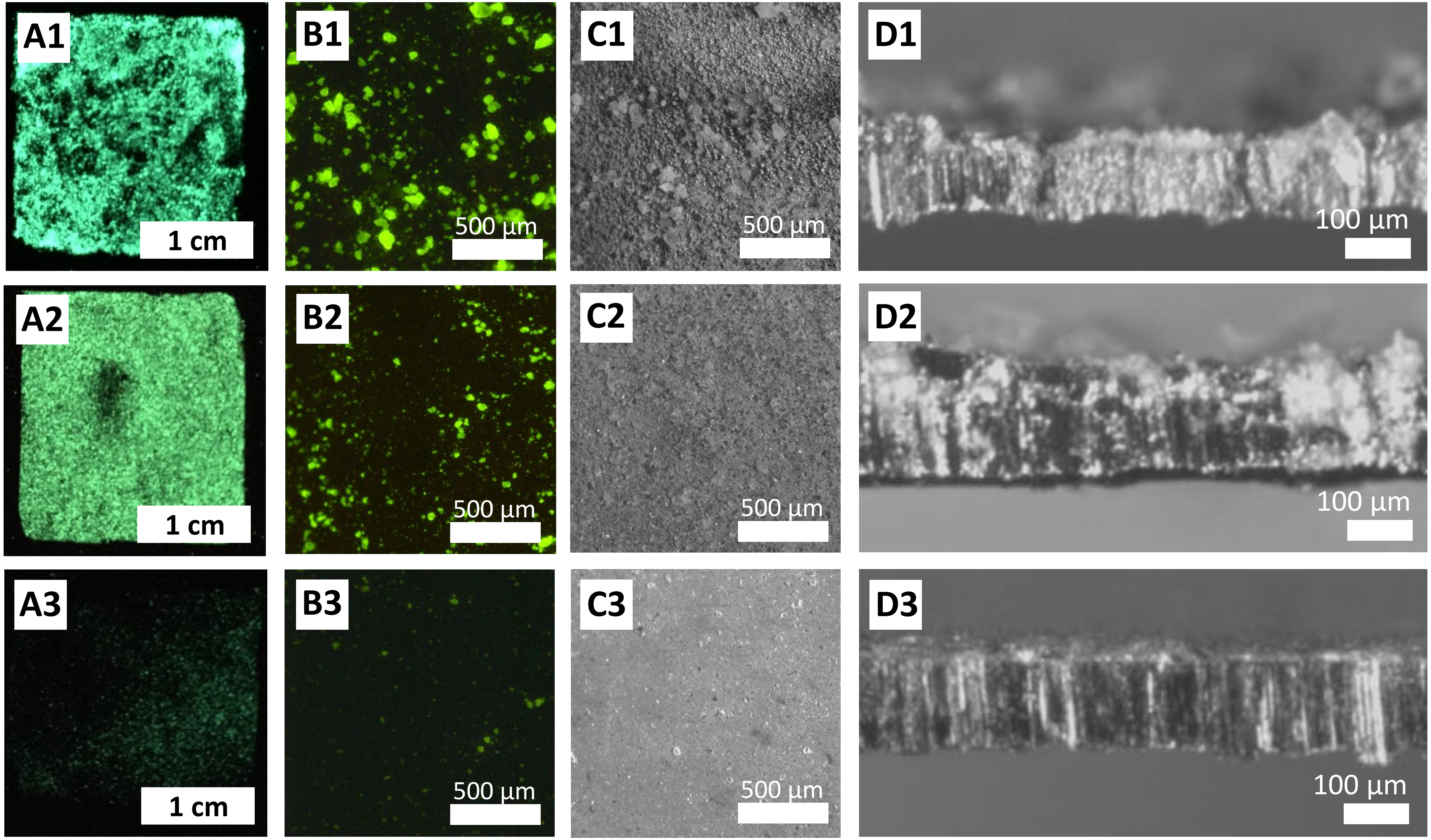
A1
1 cm
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500 µm
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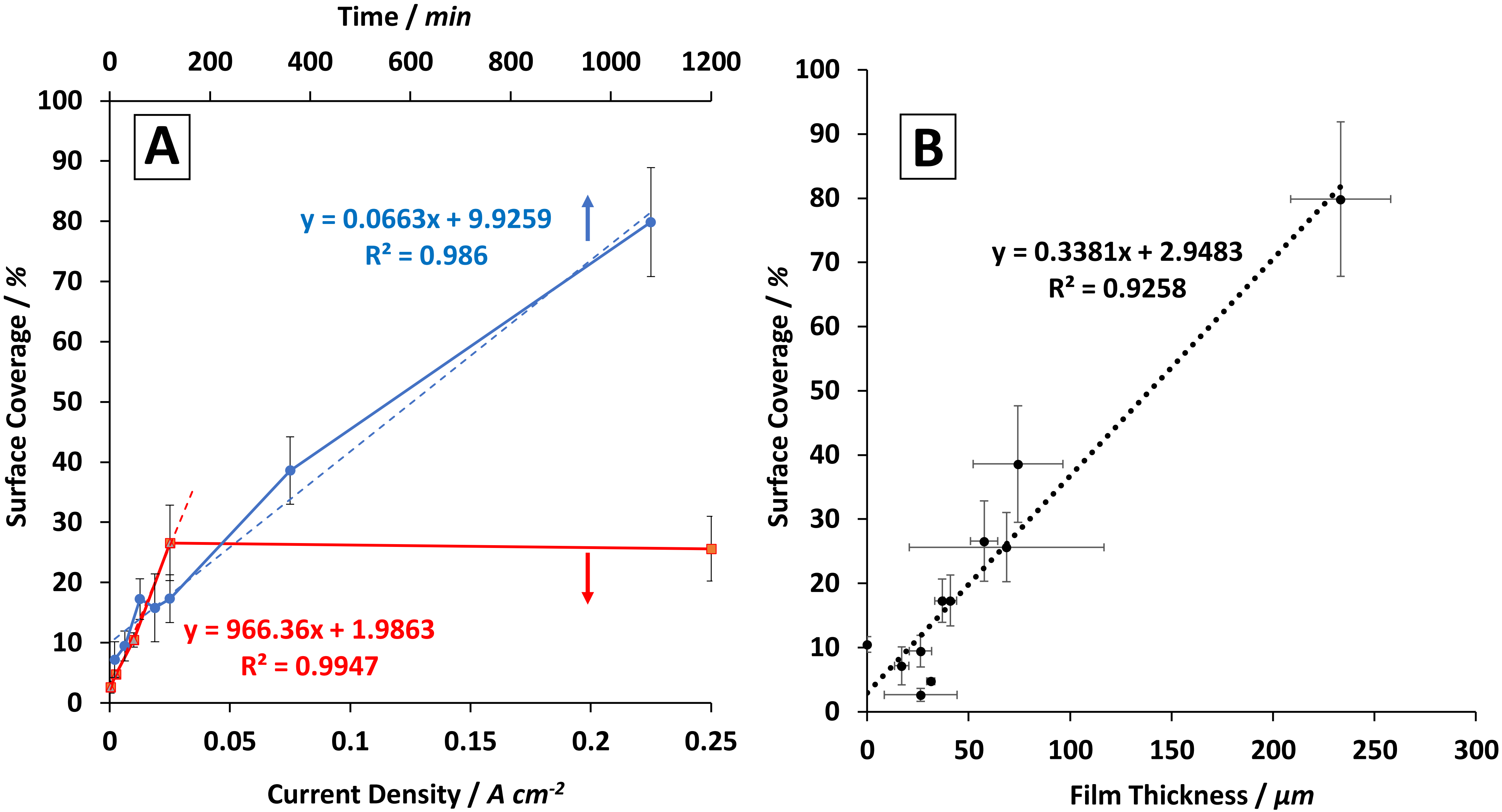
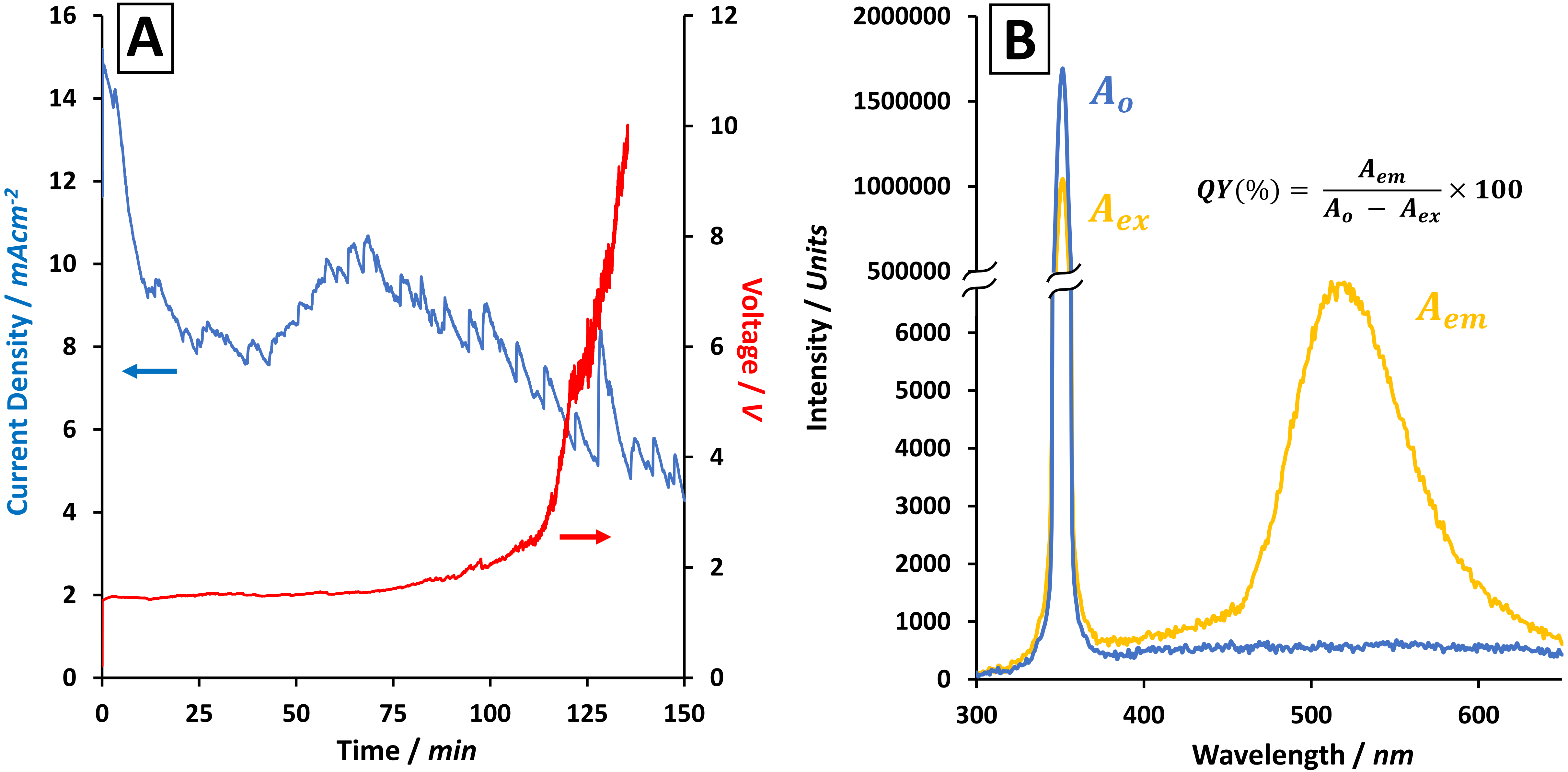

Time / *min*
0
200
400
600
800
1000
1200
100
90
80
70
60
50
40
30
20
10
0
A
y = 0.0663x + 9.9259
R² = 0.986
y = 966.36x + 1.9863
R² = 0.9947
Surface Coverage / %
0
0.05
0.1
0.15
0.2
0.25
Current Density / *A cm⁻²*
B
y = 0.3381x + 2.9483
R² = 0.9258
Surface Coverage / %
0
50
100
150
200
250
300
Film Thickness / *µm*


A
Current Density / mAcm-2
Voltage / V
Time / min
0
25
50
75
100
125
150
0
2
4
6
8
10
12
14
16
0
2
4
6
8
10
12
B
Intensity / Units
Wavelength / nm
300
400
500
600
0
1000
2000
3000
4000
5000
6000
500000
1000000
1500000
2000000
A_o
A_{ex}
A_{em}
$QY(\%) = \frac{A_{em}}{A_o - A_{ex}} \times 100$

Reagent / Parameter	**Watt's Bath Plating**[23]	**Electrostamping**[20]
$NiSO_4.6\ H_2O$ (g/L)	270	1325
$NiCl_2.6\ H_2O$ (g/L)	60	238
H_3BO_3 (g/L)	38	212
Composite ($SrAl_2O_4:Eu^{2+}$, Dy^{3+}) (g/L)	---	238
H_2O (g/L)	812	21
Cathode Current Density (A cm^{-2})	0.045	0.025
Composite Size Range (µm)	0 – 11	0 – 100
Composite Loading (%)	0 – 40	0 – 90

Name of Material/ Equipment	Company	Catalog Number
37% M Hydrochloric Acid (aq)	SigmaAldrich	320331-500ML
70% Nitric Acid (aq)	SigmaAldrich	438073-500ML
Barium magnesium aluminate, europium doped (s)	SigmaAldrich	756512-25G
Boric Acid (s)	SigmaAldrich	B6768-500G
Cotton Swab	Q-tips	Q-tips Cotton Swabs
ImageJ	National Institutes of Health	IJ 1.46r
Nickel (II) chloride hexahydrate (s)	SigmaAldrich	223387-500G
Nickel (II) sulfate hexahydrate (s)	SigmaAldrich	227676-500G
Nickel foil (s)	AliExpress	Ni99.999
Nitrile gloves	Fisher Scientific	19-149-863B
nylon membrane (s)	Tisch Scientific	RS10133
Optical Microscope equipped with FTIC filter (470 ± 20 nm)	Nikon	Eclipse 80i
Plastic Wrap	Fisher Scientific	22-305654
Porcelain Mortar	Fisher Scientific	FB961A
Porcelain Pestle	Fisher Scientific	FB961K
Potassium Hydroxide (s)	SigmaAldrich	221473-25G
Potentiostat with platinum wire	Gamry Instruments	1000E
Scoopula	Fisher Scientific	14-357Q
Spectrofluorometer	Photon Technology International	QM-40
Strontium aluminate, europium and dysprosium doped (s)	GloNation	756539-25G
Variable linear DC power supply	Tekpower	TP3005T
Yttrium oxide, europium doped (s)	SigmaAldrich	756490-25G

Comments/Description
corrosive - handle in fume hood
corrosive - handle in fume hood
fine powder
toxic
free software
toxic
toxic
corrosive
powder
fine powder

Reviewer #1:

Minor Concerns:
Abstract. "because the composite particles are either 1) not charged so they do not have a driving force to plate,... . No, the particles can be electrically uncharged - but the driving force for movement to the workpiece is often convective-diffusion, rather than migration or electrophoresis.

Thank you for this distinction. We have modified the text on line 35 by replacing:

“do not have a driving force to plate” with “do not have a strong electrostatic attraction to the cathode”

Protocol. Faraday's laws of electrolysis. Rewrite as:
n is the amount of metal deposited (units: mol)

Thank you. This change was made on line 218 by replacing:

“n is the number of moles of metal deposited” to “n is the amount of metal deposited (units: mol)”

Reviewer #3:

Major Concerns:
It would be good to determine the adhesive strength of the coating. But there is no such data. I understand that this is extra experiment, but it is important from the point of view of application.

We agree that this would be a useful characterization of this process. However, we do not have the equipment or the expertise to conduct these experiments. We have conducted a qualitative Scotch tape adhesion test (~ 15 psi, which they passed); however, this test is typically used for paints and soft surfaces. In order to match the strong adhesion that is observed for electroplated nickel (50 – 60,000 psi), we would need more specialized testing equipment. Although this experiment may be of interest in future studies, we would like to suggest that the article focuses on the novel plating method and the potential for unusually high loading of composite particles.

In addition, we have made the following change in the text to increase clarity about the attraction between the composite particle and the cathode:

Line 388 Discussion 2nd paragraph: “adhesion” replaced with “physisorption”

Minor Concerns:
1) If you use one balances You should write one resolution of weight. For example: 10.00 g NiSO4·6H2O, 2.12 g NiCl2·6H2O, 1.60 g H3BO3

The significant figures were adjusted to reflect the sensitivity of the balance by making the following changes of the masses measured:

Lines 108-125, “10”, “2.12”, “1.6”, “1.8” and “0.1875” were replaced with “10.000”, “2.120”, “1.600”, “1.800” and “0.188”

In addition, we took the opportunity to correct the following errors we found:

Line 128 replacing “mL” to “µL”
Line 364-365 replacing “over time” with “after 30 min”
Line 428 replacing “87” with “80”

2) Look fig.1: cross-sections images [D] have scale 100 mµ. If You change current density 0.25-0.025-0.01 A/cm2 and constant time 30 min the thickness of films will very different. Should check foto about correct scales or deposition time.

We agree that under typical circumstances of pure nickel plating, the thickness should scale directly with the current density at a rate of 614 µm per A cm^{-2} at 100% current efficiency. However, what we observed here is that with high surface loadings, the deposition rate decreases. This happens as the applied current increases from 0.0025 to 0.025 to 0.25 Acm^{-2} (Figure 1 D1-D3). We attribute this to the increased resistance of the overall film as the particles embed within the film. The film has increasingly higher proportions of non-charged large (87 µm) ceramic particles, and therefore fewer possible sites for nickel reduction and film growth. So, at higher currents, the thickness does not dramatically increase. We observe the same effect when increasing the deposition time.

We are confident that our microscope is calibrated with the image scale bar and that the duration of the coating is accurate. Because this is a methods-focused article, the cross-section images are representative of the type of characterization to conduct for this experiment. However, we acknowledge that this question raises an important point to be clarified in the text with the following changes:

Lines 325-330 Results 3rd paragraph: ~~Despite changes in surface morphology~~ Under optimized conditions, the current efficiencies remain high (85-95%) as calculated from Equations 1 and 2. However, at either high current densities (> 0.025 A cm^{-2}) or long durations (> 1 h), we observed a decrease in coating efficiency as the particle loading increases. For example, the film thickness of this metal composite does not increase as would be expected for pure nickel despite higher applied currents (Figure 1, D1-D3).

Lines 417-419 Discussion 2nd paragraph: “…increase the resistivity of the cathode. This effect may explain the lower than expected thicknesses as the ceramic particles occupy more of the nickel surface, decreasing the available sites for nickel reduction and film growth.

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