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Title: A Salt-Templated Synthesis Method for Porous Platinum-Based Macrobeams and Macrotubes

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Author Questionnaire

1. Microscopy: Does your protocol involve video microscopy, such as filming a complex dissection or microinjection technique? **N**

2. Software: Does the part of your protocol being filmed demonstrate software usage? **N**

3. Filming location: Will the filming need to take place in multiple locations (greater than walking distance)? **N**

Script Length

Number of shots: **59**

Introduction

1. Introductory Interview Statements

REQUIRED:

1.1. **F. John Burpo**: This protocol offers a simple, relatively fast method for synthesizing high-surface area and high aspect ratio platinum and platinum alloy macrobeams and macrotubes with a square cross-section **[1]**.

1.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

REQUIRED:

1.2. **Anchor R. Losch**: The salt-templating method allows control of the template metal ion ratio and resulting mass composition and of the macrobeam and macrotube nanostructures **[1]**.

1.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

OPTIONAL:

1.3. **Enoch A. Nagelli**: Macrobeam and macrotube pressed films may address the need for integral 3-dimensional electrodes for catalysis and sensing applications **[1]**.

1.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera *Videographer: Can cut for time*

OPTIONAL:

1.4. **F. John Burpo**: The ability of Magnus's salt derivatives to be chemically reduced to form macrobeams and macrotubes suggests that the salt-templating synthesis method may be applied to a wider-range of metal salts **[1]**.

1.4.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera *Videographer: Can cut for time*

Protocol

2. Magnus' Salt Derivative Template Preparation

2.1. To prepare Magnus' salts with a 1:0:1 platinum two-positive:platinum two-negative ratio, add 0.5 milliliters of 100-millimolar potassium tetrachloroplatinate into a microfuge tube **[1]** and forcefully pipette 0.5 milliliters of 100-millimolar tetraammineplatinum two chloride hydrate in water into the tube **[2]**.

2.1.1. WIDE: Talent adding K_2PtCl_4 to tube, with K_2PtCl_4 container visible in frame NOTE: This and next shot merged into one.

2.1.2. Talent adding $Pt(NH_3)_4Cl_2{\cdot}H_2O$ to tube, with $Pt(NH_3)_4Cl_2{\cdot}H_2O$ container visible in frame

2.2. The resulting 1-milliiter volume salt needle template solutions will exhibit an opaque light green color **[1]**.

2.2.1. Shot of solutions

2.3. To prepare a 1:1:0 platinum-palladium salt needle template, add 0.5 milliliters of tetraammineplatinum two chloride hydrate in water to a microcentrifuge tube **[1-TXT]** and forcefully pipette 0.5 milliliters of 100-millimolar sodium tetrachloropalladate to the tube **[2]**.

2.3.1. Talent adding $Pt(NH_3)_4Cl_2{\cdot}H_2O$ to tube, with $Pt(NH_3)_4Cl_2{\cdot}H_2O$ container visible in frame **TEXT: Salt template platinum-palladium ion ratios designated Pt^{2+}:Pd^{2-}:Pt^{2-}; Platinum-only salts = 1:0:1 ratio**

2.3.2. Talent adding Na_2PdCl_4 to tube, with Na_2PdCl_4 container visible in frame

2.4. To prepare a 2:1:1 platinum-palladium salt needle template, add 0.25 milliliters of 100-millimolar sodium tetrachloropalladate **[1]** and 0.25 milliliters of 100-millimolar potassium tetrachloroplatinate to a microfuge tube **[2]**.

2.4.1. Talent adding Na_2PdCl_4 to tube, with Na_2PdCl_4 container visible in frame

2.4.2. Talent adding K_2PtCl_4 to tube, with K_2PtCl_4 container visible in frame

2.5. Vortex the tube for 3-5 seconds **[1]** before forcefully pipetting 0.5 milliliters of 100-millimolar tetraammineplatinum two chloride hydrate in water to the tube **[2]**.

2.5.1. Tube being vortexed

2.5.2. Talent adding $Pt(NH_3)_4Cl_2{\cdot}H_2O$ to tube, with $Pt(NH_3)_4Cl_2{\cdot}H_2O$ container visible in frame

2.6. To prepare a 3:1:2 platinum-palladium salt needle template, pipette 0.167 milliliters of 100-millimolar sodium tetrachloropalladate **[1]** and 0.333 milliliters of 100-millimolar potassium tetrachloroplatinate to a microfuge tube **[2]**.

2.6.1. Talent adding Na_2PdCl_4 to tube, with Na_2PdCl_4 container visible in frame NOTE: This and next shot merged into one.

2.6.2. Talent adding K_2PtCl_4 to tube, with K_2PtCl_4 container visible in frame

2.7. After vortexing, forcefully pipette 0.5 milliliters of 100-millimolar tetraammineplatinum two chloride hydrate in water to the tube **[1]**.

2.7.1. Talent adding $Pt(NH_3)_4Cl_2{\cdot}H_2O$ to tube, with $Pt(NH_3)_4Cl_2{\cdot}H_2O$ container visible in frame

2.8. Salt templates with a higher platinum ratio should yield a greener color **[1]**, while templates with increasing palladium contents result in more orange, pink, and brown colors within the solution **[2]**.

2.8.1. Shot of templates with ratio labels visible in frame *Video Editor: please emphasize greener solutions*

2.8.2. Use 2.8.1. *Video Editor: please emphasize orange, pink, and/or brown solutions when mentioned*

2.9. To prepare a 1:0:1 salt ratio copper-platinum salt needle template, add 0.5 milliliters of 100 millimolar potassium tetrachloroplatinate to a microfuge tube **[1-TXT]** and forcefully add 0.5 milliliters of 100-millimolar tetraaminecopper two sulfate in water to the first tube of DMAB **[2]**.

2.9.1. Talent adding K_2PtCl_4 to tube, with K_2PtCl_4 container visible in frame **TEXT: Pt^{2-}:Pt^{2+}:Cu^{2+} ratio** NOTE: This and next shot merged into one.

2.9.2. Talent adding $Cu(NH_3)_4SO_4{\cdot}H_2O$ to tube, with $Cu(NH_3)_4SO_4{\cdot}H_2O$ container visible in frame

2.10. To prepare a 3:1:2 salt ratio copper-platinum salt needle template, add 0.167 milliliters of 100-millimolar tetraammineplatinum two chloride hydrate in water **[1]** and 0.333 milliliters of 100-millimolar of tetraaminecopper two sulfate in water to the tube **[2]**.

2.10.1. Talent adding $Pt(NH_3)_4Cl_2 \cdot H_2O$ to tube, with $Pt(NH_3)_4Cl_2 \cdot H_2O$ container visible in frame NOTE: This and next shot merged into one.
2.10.2. Talent adding $Cu(NH_3)_4SO_4 \cdot H_2O$ to tube, with $Cu(NH_3)_4SO_4 \cdot H_2O$ container visible in frame

2.11. After vortexing, forcefully add 0.5 milliliters of 100-millimolar potassium tetrachloroplatinate to the tube **[1]**.

2.11.1. Talent adding $K_2PtCl_4$to tube, with K_2PtCl_4 container visible in frame

2.12. To prepare the 2:1:1 salt ratio copper-platinum salt needle template, add 0.25 milliiters of 100-millimolar tetraammineplatinum two chloride hydrate in water **[1]** and 0.25 milliliters of 100-millimolar tetraaminecopper two sulfate in water to a microfuge tube **[2]** and vortex the microfuge tube for 3-5 seconds **[3]**.

2.12.1. Talent adding $Pt(NH_3)_4Cl_2 \cdot H_2O$ to tube, with $Pt(NH_3)_4Cl_2 \cdot H_2O$ container visible in frame NOTE: This and next shot merged into one.
2.12.2. Talent adding $Cu(NH_3)_4SO_4 \cdot H_2O$ to tube, with $Cu(NH_3)_4SO_4 \cdot H_2O$ container visible in frame
2.12.3. Tube being vortexed

2.13. Then forcefully pipette 0.5 milliliters of 100-millimolar potassium tetrachloroplatinate to the tube **[1]**.

2.13.1. Talent adding K_2PtCl_4 to tube, with K_2PtCl_4 container visible in frame

2.14. To prepare the 1:1:0 salt ratio copper-platinum salt needle template, pipette 0.5 milliliters of 100-millimolar tetraammineplatinum two chloride hydrate in water to a microfuge tube **[1]** and forcefully pipette 0.5 milliliters of 100-millimolar potassium tetrachloroplatinate into the tube to obtain a 1-milliliter salt needle template solution **[2]**.

2.14.1. Talent adding $Pt(NH_3)_4Cl_2 \cdot H_2O$ to tube, with $Pt(NH_3)_4Cl_2 \cdot H_2O$ container visible in frame NOTE: This and next shot merged into one.
2.14.2. Talent adding K_2PtCl_4 to tube, with K_2PtCl_4 container visible in frame

2.15. The combination of copper and platinum ions will result in the formation of a purple, cloudy solution that is not as opaque as the platinum and palladium solutions **[1]**.

2.15.1. Shot of purple solutions

3. Salt-Template Chemical Reduction

3.1. To perform a chemical reduction of the platinum-palladium salt templates, add 50 milliliters of 0.1-molar sodium borohydride solution into each of four 50-milliliter conical tubes **[1]** add the entire 1-milliliter volume of one platinum-palladium salt template solution to each tube **[2-TXT]**.

3.1.1. WIDE: Talent at fume hood, adding template to tube(s), with $NaBH_4$ container visible in frame
3.1.2. Talent adding Pt-Pd salt template(s) to tube(s)

3.2. To perform a chemical reduction of the copper-platinum salt templates, add 50 milliliters of 0.1-molar DMAB (D-M-A-B) solution into each of four 50-milliliter conical tubes **[1-TXT]** and add the entire 1-milliliter volume of one copper-platinum salt template solution to each tube under a fume food **[2]**.

3.2.1. Talent DMAB to tube(s), with DMAB container visible in frame **TEXT: DMAB: dimethylamine borane**
3.2.2. Talent adding Cu-Pt salt template(s) to tube(s)

3.3. After 24 hours, slowly decant the supernatant from each reduced solution into a waste container, taking care not to pour out the samples **[1]**, and transfer the precipitates into new 50-milliliter tubes **[2-TXT]**.

3.3.1. Talent decanting supernatant
3.3.2. Precipitate being added to tube **TEXT: Use spatula to dislodge salt samples as necessary**

3.4. Fill each of tube with 50 milliliters of deionized water **[1]** and incubate the tightly capped tubes for 24 hours with gentle rocking **[2]**.

3.4.1. Talent adding water to tube(s)
3.4.2. Tubes on rocker

3.5. The next day, place the tubes upright in a tube rack for 15 minutes to allow the samples to sediment **[1]** before slowly pouring off the supernatant **[2]**.

3.5.1. Talent placing tube(s) onto rack
3.5.2. Supernatant being decanted

3.6. Refill each tube with 50 milliliters of deionized water **[1]** and rock the samples for an additional 24 hours **[2]**.

3.6.1. Talent adding water to tube(s)
3.6.2. Samples on rocker

3.7. At the end of the incubation, place the tubes in a rack for 15 minutes **[1]** before decanting as much of the clear or grey supernatants as possible **[2]**.

3.7.1. Talent placing tube(s) onto rack
~~3.7.2. Supernatant being decanted~~ NOTE: Not shot but there are numerous takes of 3.5.2 that can be used here

4. Macrotube and Macrobeam Film Preparation

4.1. To prepare macrotube and macrobeam films, use a spatula to gently transfer the precipitate material from each tube onto individual glass slides **[1]** and to consolidate the samples into a uniform, approximately 0.5-millimeter-high piles **[2]**.

4.1.1. WIDE: Talent adding precipitate to slide
4.1.2. Precipitate being made into pile

4.2. Then place the slides in a location that will not be disturbed by air currents for 24 hours **[1]**.

4.2.1. Talent placing slide(s)

4.3. When the samples have dried, place a second glass slide onto each dried, reduced sample **[1]** and manually apply approximately 200 kilopascals of force to the top slide **[2]** to create a thin film of macrotubes or macrobeams on the bottom slide **[3]**.

4.3.1. Slide being placed NOTE: This and next shot merged into one.
4.3.2. Slide being pressed
4.3.3. Shot of film

5. Material Characterization

5.1. For scanning electron microscopy of the samples, use carbon tape to fix the thin film to a scanning electron microscopy sample stub **[1]** and set the initial accelerating voltage to 15 kilovolts and the beam current to 2.7-5.4 picoamps **[2]**.

5.1.1. WIDE: Talent taping sample to stub
5.1.2. Talent setting imaging parameters

5.2. Then zoom out to a large sample area **[1]** and collect an energy dispersive x-ray spectrum to quantify the elemental composition of the sample **[2]**.

5.2.1. Talent zooming out display
5.2.2. LAB MEDIA: Figure 2A

5.3. For x-ray diffractometric analysis, place the thin film sample slide onto the scanning stage **[1]** and perform x-ray diffractometry scans for diffraction angles 2 theta from 5-90 degrees at 45 kilovolts and 40 milliamps with copper K-alpha radiation, a 2 theta-step size of 0.0130 degrees, and 20 seconds per step **[2]**.

5.3.1. Talent placing sample onto scanning stage
5.3.2. Talent setting scanning parameters

6. Electrochemical Characterization

6.1. To normalize the electrochemical measurements by milligrams of active materials, transfer the samples into individual electrochemical vials **[1]** and gently add 0.5-molar sulfuric acid to each the sample for a 24-hour incubation at room temperature **[2-TXT]**.

6.1.1. WIDE: Talent adding sample to vial
6.1.2. Talent adding H_2SO_4 to vial, with H_2SO_4 container visible in frame **TEXT: Alternative: Treat with 0.5 M KCl**

6.2. The next day, place the lacquer-coated wire with a 1-millimeter exposed tip from individual 3-electrode cells in contact with the top surface of the film at the bottom of each electrochemical vial **[1-TXT]** and perform electrochemical impedance spectroscopy from 1 megahertz to 1 millihertz with a 10-millivolt sine wave at 0 volts **[2]**.

6.2.1. Talent placing wire in contact with aerogel **TEXT: See text for 3-electrode cell details**
6.2.2. Talent setting EIS parameters

6.3. Then perform cyclic voltammetry using a voltage range of -0.2 to 1.2 volts with scan rates of 10, 25, 50, 75, and 100 millivolts/second **[1]**.

6.3.1. Talent setting cyclic voltammetry parameters

Protocol Script Questions

A. Which steps from the protocol are the most important for viewers to see?

n/a

B. What is the single most difficult aspect of this procedure and what do you do to ensure success?

n/a

Results

7. Results: Representative Platinum-Based Marcobeam and Marcotube Analyses

7.1. The addition of oppositely charged square planar noble metal ions **[1]** results in near instantaneous formation of high aspect ratio salt crystals **[2]**.

7.1.1. LAB MEDIA: Figure 1 *Video Editor: please emphasize column of formulas*
7.1.2. LAB MEDIA: Figure 1 *Video Editor: please emphasize column of images*

7.2. The chemical reduction of Magnus' salts formed with a 1:1 ratio of platinum-positive:platinum-negative ions and reduced with sodium borohydride results in macrotubes with a generally hollow inner cavity and porous side wells **[1]**.

7.2.1. LAB MEDIA: Figure 2

7.3. The macrotubes generally conform to the geometry of the salt needle templates **[1]** with flat sidewalls **[2]** and a square cross section **[3]**.

7.3.1. LAB MEDIA: Figures 2A and 2B
7.3.2. LAB MEDIA: Figures 2A and 2B *Video Editor: please emphasize flat side wall in Figure 2B*
7.3.3. LAB MEDIA: Figures 2A and 2B *Video Editor: please emphasize cross section in Figure 2B*
7.3.4.

7.4. DMAB-reduced copper-platinum macrotubes **[1]** present the most distinct and largest square cross sections, with approximately 3-micrometer sides **[2]**.

7.4.1. LAB MEDIA: Figures 4A-4C
7.4.2. LAB MEDIA: Figure 4A-4C *Video Editor: please emphasize cross section in Figure 4A*

7.5. The DMAB-reduced copper-platinum macrotube sidewalls also demonstrate a highly textured surface without a significant porosity **[1]**.

7.5.1. LAB MEDIA: Figures 4A-4C *Video Editor: please emphasize sidewall in Figure 4B*

7.6. Platinum and platinum-palladium macrotube and macrobeam chemical composition can be initially characterized with x-ray diffraction **[1]**.

7.6.1. LAB MEDIA: Figures 5A and 5B

7.7. X-ray diffraction analysis of DMAB-reduced macrotubes reveals superimposed peaks **[1]** that shift toward either platinum **[2]** or copper depending on the relative salt template stoichiometry, suggesting an alloy composition **[3]**.

7.7.1. LAB MEDIA: Figure 5C
7.7.2. LAB MEDIA: Figure 5C *Video Editor: please emphasize purple and green data lines*
7.7.3. LAB MEDIA: Figure 5C *Video Editor: please emphasize blue and red data lines*

7.8. Sodium borohydride-reduced copper-platinum macrobeams **[1]** exhibit distinct copper **[2]** and platinum x-ray diffraction peaks, suggesting a bi-metallic composition **[3]**.

7.8.1. LAB MEDIA: Figure 5D
7.8.2. LAB MEDIA: Figure 5D *Video Editor: please emphasize blue and red data lines*
7.8.3. LAB MEDIA: Figure 5D *Video Editor: please emphasize purple and green data lines*

7.9. X-ray photoelectron spectra for platinum macrotubes **[1]** indicate little evidence of an oxide species, suggesting a catalytically active surface **[2]**.

7.9.1. LAB MEDIA: Figure 6A
7.9.2. LAB MEDIA: Figure 6A *Video Editor: please emphasize blue and red peaks*

7.10. X-ray photoelectron spectra for platinum-palladium macrobeams also present no indication of metal oxide context **[1]**.

7.10.1. LAB MEDIA: Figure 6B

Conclusion

8. Conclusion Interview Statements

8.1. **Anchor R. Losch**: While the pressed films can be manipulated with tweezers, care must be taken when transferring the films into the electrochemical vials to prevent fracturing **[1]**.

8.1.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera

8.2. **Enoch A. Nagelli**: Given the ability to press the macrobeams and macrotubes into integral films, mechanical characterization to determine elastic and flexural moduli can also be performed **[1]**.

8.2.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera *Videographer: Can cut for time*

8.3. **F. John Burpo**: Salt-templates for the synthesis of porous, high surface area materials should enable researchers to explore a wider range of metal salts and resulting metal, alloy, and multi-metallic materials **[1]**.

8.3.1. INTERVIEW: Named talent says the statement above in an interview-style shot, looking slightly off-camera *Videographer: Can cut for time*