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## Salt-Templated Synthesis Method for Porous Platinum-based Macrobeams and Macrotubes

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**TITLE:**  
A Salt-Templated Synthesis Method for Porous Platinum-based Macrobeams and Macrotubes

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**KEYWORDS:**  
porous, nanoparticle, noble metal, platinum, palladium, copper, catalysis, macrotube, macrobeam, nanotube

**SUMMARY:**  
A synthesis method to obtain porous platinum-based macrotubes and macrobeams with a square



cross section through chemical reduction of insoluble salt-needle templates is presented.

#### **ABSTRACT:**

The synthesis of high surface area porous noble metal nanomaterials generally relies on time consuming coalescence of pre-formed nanoparticles, followed by rinsing and supercritical drying steps, often resulting in mechanically fragile materials. Here, a method to synthesize nanostructured porous platinum-based macrotubes and macrobeams with a square cross section from insoluble salt needle templates is presented. The combination of oppositely charged platinum, palladium, and copper square planar ions results in the rapid formation of insoluble salt needles. Depending on the stoichiometric ratio of metal ions present in the salt-template and the choice of chemical reducing agent, either macrotubes or macrobeams form with a porous nanostructure comprised of either fused nanoparticles or nanofibrils. Elemental composition of the macrotubes and macrobeams, determined with x-ray diffractometry and x-ray photoelectron spectroscopy, is controlled by the stoichiometric ratio of metal ions present in the salt-template. Macrotubes and macrobeams may be pressed into free standing films, and the electrochemically active surface area is determined with electrochemical impedance spectroscopy and cyclic voltammetry. This synthesis method demonstrates a simple, relatively fast approach to achieve high-surface area platinum-based macrotubes and macrobeams with tunable nanostructure and elemental composition that may be pressed into free-standing films with no required binding materials.

#### **INTRODUCTION:**

Numerous synthesis methods have been developed to obtain high surface area, porous platinum-based materials primarily for catalysis applications including fuel cells<sup>1</sup>. One strategy to achieve such materials is to synthesize monodisperse nanoparticles in the form of spheres, cubes, wires, and tubes<sup>2-5</sup>. To integrate the discrete nanoparticles into a porous structure for a functional device, polymeric binders and carbon additives are often required<sup>6,7</sup>. This strategy requires extra processing steps, time, and can lead to a decrease in mass specific performance, as well as agglomeration of nanoparticles during extended device use<sup>8</sup>. Another strategy is to drive the coalescence of synthesized nanoparticles into a metal gel with subsequent supercritical drying<sup>9-11</sup>. While advancements in the sol-gel synthesis approach for noble metals has reduced gelation time from weeks to as fast as hours or minutes, the resulting monoliths tend to be mechanically fragile impeding their practical use in devices<sup>12</sup>.

Platinum-alloy and multi-metallic 3-dimensional porous nanostructures offer tunability for catalytic specificity, as well as address the high cost and relative scarcity of platinum<sup>13,14</sup>. While there have been numerous reports of platinum-palladium<sup>15,16</sup> and platinum-copper<sup>17-19</sup> discrete nanostructures, as well as other alloy combinations<sup>20</sup>, there have been few synthesis strategies to achieve a solution-based technique for 3-dimensional platinum alloy and multi-metallic structures.

Recently we demonstrated the use of high concentration salt solutions and reducing agents to rapidly yield gold, palladium, and platinum metal gels<sup>21,22</sup>. The high concentration salt solutions and reducing agents were also used in synthesizing biopolymer noble metal composites using

gelatin, cellulose, and silk<sup>23-26</sup>. Insoluble salts represent the highest concentrations of ions available to be reduced and were used by Xiao and colleagues to demonstrate the synthesis of 2-dimensional metal oxides<sup>27,28</sup>. Extending on the demonstration of porous noble metal aerogels and composites from high concentration salt solutions, and leveraging the high density of available ions of insoluble salts, we used Magnus' salts and derivatives as shape templates to synthesize porous noble metal macrotubes and macrobeams<sup>29-32</sup>.

Magnus' salts assemble from the addition of oppositely charged square planar platinum ions  $[\text{PtCl}_4]^{2-}$  and  $[\text{Pt}(\text{NH}_3)_4]^{2+}$ <sup>33</sup>. In a similar manner, Vauquelin's salts form from the combination of oppositely charged palladium ions,  $[\text{PdCl}_4]^{2-}$  and  $[\text{Pd}(\text{NH}_3)_4]^{2+}$ <sup>34</sup>. With precursor salt concentrations of 100 mM, the resulting salt crystals form needles 10s to 100s of micrometers long, with square widths approximately 100 nm to 3  $\mu\text{m}$ . While the salt-templates are charge neutral, varying the Magnus' salt derivatives stoichiometry between ion species, to include  $[\text{Cu}(\text{NH}_3)_4]^{2+}$ , allows control over the resulting reduced metal ratios. The combination of ions, and the choice of chemical reducing agent, result in either macrotubes or macrobeams with a square cross section and a porous nanostructure comprised of either fused nanoparticles or nanofibrils. Macrotubes and macrobeams were also pressed into free standing films, and electrochemically active surface area was determined with electrochemical impedance spectroscopy and cyclic voltammetry. The salt-template approach was used to synthesize platinum macrotubes<sup>29</sup>, platinum-palladium macrobeams<sup>31</sup>, and in an effort to lower material costs and tune catalytic activity by incorporating copper, copper-platinum macrotubes<sup>32</sup>. The salt-templating method was also demonstrated for Au-Pd and Au-Pd-Cu binary and ternary metal macrotubes and nanofoams<sup>30</sup>.

Here, we present a method to synthesize platinum, platinum-palladium, and copper-platinum bimetallic porous macrotubes and macrobeams from insoluble Magnus' salt needle templates<sup>29,31,32</sup>. Control of the ion stoichiometry in the salt needle templates provides control over resulting metal ratios after chemical reduction and can be verified with x-ray diffractometry and x-ray photoelectron spectroscopy. The resulting macrotubes and macrobeams may be assembled and formed into a free-standing film with hand pressure. The resulting films exhibit high electrochemically active surface areas (ECSA) determined by electrochemical impedance spectroscopy and cyclic voltammetry in  $\text{H}_2\text{SO}_4$  and  $\text{KCl}$  electrolyte. This method provides a synthesis route to control platinum-based metal composition, porosity, and nanostructure in a rapid and scalable manner that may be generalizable to a wider range of salt-templates.

## PROTOCOL:

CAUTION: Consult all relevant chemical safety data sheets (SDS) before use. Use appropriate safety practices when performing chemical reactions, to include the use of a fume hood and personal protective equipment. Rapid hydrogen gas evolution during electrochemical reduction can cause high pressure in reaction tubes causing caps to pop and solutions to spray out. Ensure that reaction tube caps remain open as specified in the protocol. Conduct all electrochemical reductions in a fume hood.

## 1. Magnus' salt derivatives template preparation

NOTE: All salt templates should be chemically reduced within a few hours after preparation as prolonged storage results in a degradation of salt structure. This method describes each platinum-based macrotube and macrobeam product. To obtain additional specific product yield, conduct the method with replicate sets of salt template and reducing agent solutions.

### 1.1. Prepare metal salt solutions.

1.1.1. Add 0.4151 g of  $\text{K}_2\text{PtCl}_4$  to 10 mL of deionized water to prepare a 0.1 M (100 mM) solution of " $\text{Pt}^{2-}$ ".

1.1.2. Add 0.3521 g of  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  to 10 mL of deionized water to prepare a 0.1 M (100 mM) solution of " $\text{Pt}^{2+}$ ".

1.1.3. Add 0.2942 g of  $\text{Na}_2\text{PdCl}_4$  to 10 mL of deionized water to prepare a 0.1 M (100 mM) solution of " $\text{Pd}^{2-}$ ".

1.1.4. Add 0.2458 g of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  to 10 mL of deionized water to prepare a 0.1 M (100 mM) solution of " $\text{Cu}^{2+}$ ".

1.1.5. Vigorously shake and vortex platinum and copper salt solutions to aid in the dissolution of the salts until they are fully dissolved.

### 1.2. Prepare platinum salt needle templates.

1.2.1. To prepare Magnus' salts with a 1:1  $\text{Pt}^{2+}:\text{Pt}^{2-}$  ratio, pipette 0.5 mL of 100 mM  $\text{K}_2\text{PtCl}_4$  into a microfuge tube. Forcefully pipette 0.5 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  into the microfuge tube for a total of 1 mL of salt needle template solution.

NOTE: The solution will present an opaque light green color. The use of 50 mM  $\text{K}_2\text{PtCl}_4$  and  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  will result in longer and wider salt needles for larger platinum macrotubes after chemical reduction<sup>29</sup>. Forceful pipetting is dispensing the full reagent volume within 1 s to ensure rapid mixing of chemicals within microfuge tubes.

### 1.3. Prepare platinum-palladium salt needle templates.

NOTE: Salt template platinum-palladium ion ratios are designated as  $\text{Pt}^{2+}:\text{Pd}^{2-}:\text{Pt}^{2-}$ . The platinum-only salts prepared in Step 1.2.1. equate to a 1:0:1 ratio.

1.3.1. To prepare the salt ratio 1:1:0, pipette 0.5 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  into a microfuge tube. Forcefully pipette 0.5 mL of 100 mM  $\text{Na}_2\text{PdCl}_4$  into the microfuge tube for a total of 1 mL of salt needle template solution.

1.3.2. To prepare the salt ratio 2:1:1, pipette 0.25 mL of 100 mM  $\text{Na}_2\text{PdCl}_4$  and 0.25 mL of 100 mM of  $\text{K}_2\text{PtCl}_4$  in a microfuge tube. Vortex the microfuge tube for 3-5 s. Then forcefully pipette 0.5 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  into the microfuge tube for a total of 1 mL of salt needle template solution.

1.3.3. To prepare a 3:1:2 salt template solution, pipette 0.167 mL of 100 mM  $\text{Na}_2\text{PdCl}_4$  and 0.333 mL of 100 mM of  $\text{K}_2\text{PtCl}_4$  into a microfuge tube. Vortex the microfuge tube for 3-5 s. Then forcefully pipette 0.5 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  into the microfuge tube for a total of 1 mL salt needle template solution.

NOTE: The higher ratio of platinum in the salt templates should yield a greener color, while increasing palladium content results in more orange, pink, and brown color in the solution. Solutions will be opaque in appearance.

#### 1.4. Prepare copper-platinum salt needle templates.

NOTE: Salt template copper-platinum ion ratios are designated as  $\text{Pt}^{2+}:\text{Pt}^{2+}:\text{Cu}^{2+}$ . The 1:1:0 ratio equates to the platinum-only salts prepared in Step 1.2.1.

1.4.1. To prepare the salt ratio 1:0:1, pipette 0.5 mL of 100 mM  $\text{K}_2\text{PtCl}_4$  into a microfuge tube. Forcefully pipette 0.5 mL of 100 mM  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  into the microfuge tube for a total of 1 mL of salt needle template solution.

1.4.2. To prepare the salt ratio 3:1:2, pipette 0.167 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  and 0.333 mL of 100 mM of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  into a microfuge tube. Vortex the microfuge tube for 3-5 s. Then forcefully pipette 0.5 mL of 100 mM  $\text{K}_2\text{PtCl}_4$  into the microfuge tube for a total of 1 mL of salt needle template solution.

1.4.3. To prepare the salt ratio 2:1:1, pipette 0.25 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  and 0.25 mL of 100 mM of  $\text{Cu}(\text{NH}_3)_4\text{SO}_4 \cdot \text{H}_2\text{O}$  into a microfuge tube. Vortex the microfuge tube for 3-5 s. Then forcefully pipette 0.5 mL of 100 mM  $\text{K}_2\text{PtCl}_4$  into the microfuge tube for a total of 1 mL salt needle template solution.

1.4.4. To prepare the salt ratio 1:1:0, pipette 0.5 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  into a microfuge tube. Forcefully pipette 0.5 mL of 100 mM  $\text{K}_2\text{PtCl}_4$  into the microfuge tube for a total of 1 mL salt needle template solution.

NOTE: The combination of copper and platinum ions forms a purple, cloudy solution that is not as opaque as the solutions of steps 1.2 and 1.3. Leaving solutions of Magnus' salts for 24 hours or longer will cause the templates to degrade and change to a purple-grey or black color.

#### 1.5. Polarized optical microscope (POM) imaging of salt needle templates

1.5.1. Pipette 0.05 mL of salt template solutions prepared in Steps 1.2 – 1.4 onto a glass slide and

mount on the stage of a polarized optical microscope. Adjust the focus onto salt needles and rotate cross polarizers until the background is black.

NOTE: If salt solutions do not present needle-like structures with POM imaging, verify the water quality used for salt solution preparation. Salt needle formation is sensitive to both high and low pH.

## 2. Salt-template chemical reduction

NOTE: DMAB is toxic. Avoid breathing dust and skin contact by wearing PPE and conduct all associated tasks in a fume hood.

### 2.1. Prepare reducing agent solutions.

2.1.1. Add 0.7568 g of sodium borohydride ( $\text{NaBH}_4$ ) to 200 mL of deionized water in a 500 mL beaker to prepare a 0.1 M (100 mM)  $\text{NaBH}_4$  solution. Stir solution with a spatula until the  $\text{NaBH}_4$  is fully dissolved.

2.1.2. Pour 50 mL of 0.1 M  $\text{NaBH}_4$  solution into a 50 mL conical tube. Repeat 3x.

2.1.3. Add 1.1768 g of dimethylamine borane (DMAB) to 200 mL of deionized water in a 500 mL beaker to prepare a 0.1 M (100 mM) DMAB solution.

2.1.4. Pour 50 mL of 0.1 M DMAB solution into into a 50 mL conical tube. Repeat 3x.

### 2.2. Adding salts to reducing agent solutions

2.2.1. In a fume hood, pipette the entire 1 mL volume of each of the salt template solutions from Steps 1.2 and 1.3 into each of 4 x 50 mL conical tubes of 0.1 M  $\text{NaBH}_4$  reducing agent. Allow the chemical reduction to continue for 24 h with the cap off the tube.

2.2.2. In a fume hood, pipette the entire 1 mL volume of each of the salt template solutions from Step 1.4 into each of 4 x 50 mL conical tubes of 0.1 M DMAB reducing agent. Allow the electrochemical reduction to continue for 24 h with the cap off the tube.

NOTE: Upon the addition of the 1 mL of Magnus' salts, the reducing agent will turn a cloudy-black color and begin to vigorously form hydrogen gas. Leaving the conical tube caps off prevents the buildup of hydrogen gas pressure and potential explosion and spraying of the solutions. Loose parafilm or foil may be placed over the tubes if dust contamination is a concern.

### 2.3. Rinsing reduced macrotubes and macrobeams

2.3.1. After 24 hours of reduction, slowly decant the supernatant of each of the reduced 50 mL chemical reducing solutions into a waste container and ensure not to pour the samples out of

the tubes.

2.3.2. Pour each of the precipitates into new 50 mL conical tubes. The use of a spatula may be required to dislodge sample adhering to the tube sidewalls. Fill each of the new tubes with 50 mL of deionized water and place on a rocker with tube caps secured at a low setting for 24 h.

2.3.3. Remove the tubes from the rocker and place upright in a test tube rack for 15 min to allow the samples to sediment. Slowly pour the supernatant off the top of the tube sample into a waste container. Refill tube with 50 mL of deionized water and place on a rocker with tube caps secured for an additional 24 h.

2.3.4. Remove tubes from the rocker and place upright in a test tube rack for 15 min. Pour the supernatant off the top of the tube into a waste container.

NOTE: The supernatant will be a clear or grey color and the precipitate will be a black and generally sediment to the bottom of the conical tubes. If pouring the supernatant agitates and resuspends the reduced product, place the tube upright in a rack and wait approximately 15 minutes before pouring again. A small volume of water will remain mixed with the product.

### 3. Prepare macrotube and macrobeam films

#### 3.1. Drying of the samples on glass slides

3.1.1. Pipette as much supernatant as possible out of the 50 mL tubes without removing the reduction product.

3.1.2. Using a spatula, gently transfer the precipitate material to a glass slide. Using a spatula, consolidate the sample into a pile with uniform height of approximately 0.5 mm.

NOTE: The more water that is removed from the 50 mL tube sample prior to transferring the reduced material to the glass slide, the easier the transfer is. This makes the material behave more like a paste. Sample consolidation and uniform height aids in pressing films after drying.

3.1.3. Place glass slides with the reduced samples in a location that will not be disturbed by air currents. Dry samples for 24 h at ambient temperature.

NOTE: If more sample is needed for x-ray diffraction (XRD), scanning electron microscopy (SEM), cyclic voltammetry (CV), or other testing, multiple reduced samples from the same salt ratio may be consolidated on the same glass slide for drying.

#### 3.2. Pressing of samples and massing the materials

3.2.1. Place a second glass slide on top of a slide with dried mass of reduced samples. With fingers, press down on the glass slide above the material with ample force (approximately 200

kPa) to form a thin film of macrotubes or macrobeams.

NOTE: Pressing the reduced material between glass slides should result in a free-standing film. Occasionally pressing the dried mass of macrotubes or macrobeams results in multiple film fragments. Films can be trimmed by pressing down with a razor blade.

#### 4. Material and electrochemical characterization

4.1. Scanning electron microscopy (SEM): Affix a thin film or loose powder sample with carbon tape on a SEM sample stub. Initially use an accelerating voltage of 15 kV and beam current of 2.7 - 5.4 pA to perform imaging. Zoom out to a large sample area and collect an energy dispersive x-ray (EDS) spectra to quantify elemental composition.

4.2. X-ray diffractometry (XRD): Place the macrotube or macrobeam dried sample in a sample holder. Alternatively, place a thin film sample section, as in Step 4.1, on a glass slide. Perform XRD scans for diffraction angles  $2\theta$  from  $5^\circ$  to  $90^\circ$  at 45 kV and 40 mA with Cu  $K_\alpha$  radiation ( $1.54060 \text{ \AA}$ ), a  $2\theta$  step size of  $0.0130^\circ$ , and 20 s per step.

NOTE: XRD can be done for either the pressed or un-pressed samples. Powder sample holders typically require a significant volume of materials and the use of pressed thin films is recommended.

4.3. X-ray photoelectron microscopy (XPS): Use a monochromated Al  $K_\alpha$  source with a  $100 \text{ }\mu\text{m}$  spot size, 25 W x-ray beam and  $45^\circ$  take-off angle, an operating pressure  $< 6 \times 10^{-6} \text{ Pa}$ . Neutralize surface charging with a low-voltage Ar-ion beam and a barium oxide electron neutralizer. Set analyzer pass energy to 55 eV for high-resolution scans.

#### 4.4. Electrochemical characterization

4.4.1. Measure the mass of pressed film samples to normalize electrochemical measurements by milligrams of active materials.

4.4.2. Transfer film samples into an electrochemical vial using either flat tweezers or by gently sliding the film from a glass slide onto the inner sidewall of the vial. Gently pipette 0.5 M  $\text{H}_2\text{SO}_4$  or 0.5 M KCl electrolyte over the films samples and let sit for 24 hours.

4.4.3. Use a 3-electrode cell with a Ag/AgCl (3 M NaCl) reference electrode, a 0.5 mm diameter Pt wire auxiliary/counter electrode, and a lacquer coated 0.5 mm diameter platinum working electrode. Place the lacquer coated wire with a 1 mm exposed tip in contact with the top surface of the aerogel at the bottom of the electrochemical vial<sup>22</sup>.

4.4.4. Perform electrochemical impedance spectroscopy (EIS) from 1 MHz to 1 mHz with a 10 mV sine wave at 0 V (vs. Ag/AgCl).

4.4.5. Perform cyclic voltammetry (CV) using a voltage range of  $-0.2$  to  $1.2$  V (vs. Ag/AgCl) with scan rates of 10, 25, 50, 75, and  $100\text{ mVs}^{-1}$ .

#### REPRESENTATIVE RESULTS:

The addition of oppositely charged square planar noble metal ions results in near instantaneous formation of high aspect ratio salt crystals. The linear stacking of square planar ions is shown schematically in **Figure 1**, with the polarized optical microscopy images revealing salt needles that are 10's to 100's of micrometers long. A concentration of 100 mM was used for all platinum, palladium, and copper salt solutions. While the salt needle templates are charge neutral in that the total cation and anion charges are equal, the stoichiometry of the resulting salt needles can be varied with a tertiary combination of ions. For instance, platinum palladium salt template stoichiometry was varied with  $\text{Pt}^{2+}:\text{Pd}^{2-}:\text{Pt}^{2-}$  ratios of 1:1:0, 2:1:1, 3:1:2 for a relative platinum-to-palladium ratio of 1:1, 3:1, and 5:1, respectively. In a similar manner,  $\text{Pt}^{2-}:\text{Pt}^{2+}:\text{Cu}^{2+}$  ratios of 1:0:1, 3:1:2, 2:1:1, and 1:1:0 resulted in Pt:Cu ratios of 1:1, 2:1, 3:1, and 1:0, respectively. The average length of the salt needles varied depending on the ratio of dissimilar ions.

The chemical reduction of Magnus' salts, formed with a 1:1 ratio of  $\text{Pt}^{2+}:\text{Pt}^{2-}$  ions, with  $\text{NaBH}_4$  results in macrotubes with a generally hollow inner cavity and porous side wells shown schematically in **Figure 1A** and seen in the scanning electron micrographs in **Figure 2**. In **Figure 2A-B**, the macrotubes are seen to generally conform to the geometry of the salt needle templates with flat sidewalls and a square cross section. The macrotube sidewalls shown in **Figure 2C** appear to consist of fused nanoparticles on the order of 100 nm, but at higher magnification in **Figure 2D**, these nanoparticles appear to exhibit fused nanofibrils approximately 4-5 nm in diameter. Reduction of salts formed with different ratios of  $\text{Pt}^{2+}:\text{Pd}^{2-}:\text{Pt}^{2-}$  with dimethylamine borane (DMAB) results in macrobeams with no hollow cavity, but rather a porous nanostructure throughout the square cross sectional area shown schematically in **Figure 1B** and seen in the electron micrographs in **Figure 3**. With a  $\text{Pt}^{2+}:\text{Pd}^{2-}:\text{Pt}^{2-}$  ratio of 1:1:0, the macrobeams exhibit a nanostructure of fused nanofibrils 4-7 nm diameter seen in **Figure 3A-B** similar to the sidewall features seen in platinum macrotubes in **Figure 2D**. A  $\text{Pt}^{2+}:\text{Pd}^{2-}:\text{Pt}^{2-}$  ratio of 2:1:1 presents compact nanoparticles 8-16 nm both on the macrobeam surface, as well as throughout the square cross section seen in **Figure 3C-D**. The chemically reduced 3:1:2  $\text{Pt}^{2+}:\text{Pd}^{2-}:\text{Pt}^{2-}$  salt ratio seen in **Figure 3E-F** exhibits macrobeams with nanoparticles similar to the 2:1:1 ratio though with a lesser density and higher porosity throughout the square cross section.

Reduction of  $\text{Pt}^{2-}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salts with DMAB results in macrotubes with a hollow cavity, whereas the use of  $\text{NaBH}_4$  as the reducing agent results in macrobeams with a porous cross section shown schematically in **Figure 1C**. The DMAB reduced  $\text{Pt}^{2-}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salts are shown in **Figure 4**. The macrotubes seen in **Figure 4A-C** reduced from 1:0:1  $\text{Pt}^{2-}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salt needles present the most distinct and largest square cross section with approximately  $3\text{ }\mu\text{m}$  sides. Macrotube sidewalls present a highly textured surface, though unlike the platinum and platinum-palladium macrotube and macrobeam sidewalls seen in **Figure 2** and **Figure 3**, without significant porosity. Macrotubes formed from 3:1:2 and 2:1:1 salt templates in **Figure 4D-F** and **Figure 4G-I**, respectively, reveal hollow cores with a cross section approximately 200 nm square and interconnected nanoparticle porous sidewalls from the exterior of the macrotubes to the inner cavity. A  $\text{Pt}^{2-}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salt



teemplate with 1:1:0 ratio (which is the same template used for platinum macrotubes reduced with  $\text{NaBH}_4$ ) reduced with DMAB results in linear aggregations of nanoparticles generally conforming to the high aspect ratio salt-template, though with no hollow cavity as seen in **Figure 4J-L**.

Macrotube and macrobeam chemical composition was initially characterized with XRD shown in **Figure 5**, where salt template stoichiometry ratios are shown in **Figures 5B-D**. Platinum macrotubes in **Figure 5A** indexed to Joint Committee on Powder Diffraction Standards (JCPDS) reference number 01-087-0640. Platinum-palladium macrobeams indexed to JCPDS reference numbers 03-065-6418 for platinum-palladium alloy, 00-004-0802 for platinum, and 01-087-0643 for palladium in **Figure 5B**. Copper-platinum peaks indexed to JCPDS reference number 01-087-0640 for platinum and 03-065-9026 for copper, however, DMAB reduction to macrotubes indicates XRD superimposed peaks that shift toward either platinum or copper depending on the relative salt template stoichiometry as shown in **Figure 5C** suggesting alloy composition.  $\text{NaBH}_4$  reduced copper-platinum macrobeams exhibit distinct copper and platinum XRD peaks suggesting a bi-metallic composition seen in **Figure 5D**.

X-ray photoelectron spectra are shown for platinum, platinum-palladium, and copper-platinum macrotubes and macrobeams in **Figure 6**. Platinum macrotubes indicate little evidence of oxide species in **Figure 6A** suggesting a catalytically active surface. The XPS spectra for platinum-palladium macrobeams in **Figure 6B-C** also presents no indication of metal oxide context. **Figure 6D-E** shows the XPS spectra for DMAB reduced copper-platinum macrotubes suggesting predominantly metallic copper and platinum, with the presence of  $\text{Cu}_2\text{O}$  only in the 1:0:1  $\text{Pt}^{2+}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salt-template sample. Bulk metal compositions were also determined using energy dispersive x-ray spectroscopy (EDS). The tabulated results comparing salt stoichiometry, EDS and XPS compositions for platinum-palladium and copper-platinum macrotubes and macrobeams are shown in **Table 1** and **Table 2**, respectively. In general, salt stoichiometry correlates with the bulk metal composition indicated with EDS, though XPS reveals a surface enrichment for platinum for both platinum-palladium and copper-platinum structures likely due to a reduction-dissolution mechanism described in the Discussion section. For platinum-palladium macrobeams EDS determined Pt:Pd composition indicates 6.35:1, 3.50:1, 1.12:1 for the 3:1:2, 2:1:1, 1:1:0 salt-template ratios, respectively. XPS Pt:Pd ratios show the same general trend with 11.7:1, 6.45:1, and 1.89:1 for the 3:1:2, 2:1:1, 1:1:0 salt ratios, respectively. Copper-platinum macrotubes and macrobeams reduced with DMAB and  $\text{NaBH}_4$ , respectively, show the same general trend between EDS and XPS determined metal compositions as seen in **Table 2**.

As an example of electrochemical characterization of pressed macrotube and macrobeam films, **Figure 7A** shows platinum macrotubes pressed into a free-standing film. Electrochemical impedance spectroscopy in 0.5 M KCl electrolyte is shown in **Figure 7B** across a frequency range of 100 kHz to 1 mHz, with the high frequency range shown in the inset. The specific capacitance of the platinum macrotube film is estimated from the lowest frequency in the specific capacitance ( $C_{\text{sp}}$ ) versus log (frequency) plot in **Figure 7C**. The estimated  $C_{\text{sp}}$  is  $18.5 \text{ Fg}^{-1}$  with a corresponding solvent accessible specific surface area of  $61.7 \text{ m}^2\text{g}^{-1}$ . **Figure 7D** shows the cyclic voltammetry curves in  $\text{H}_2\text{SO}_4$  electrolyte at scan rates of 0.5, 1, 5, and  $10 \text{ mVs}^{-1}$ . The  $0.5 \text{ mVs}^{-1}$

scan is highlighted in **Figure 7E** exhibiting characteristic hydrogen adsorption and desorption peaks at potentials less than 0 V (vs Ag/AgCl) and an oxidative toe region and reduction peaks greater than 0.5 V (vs (Ag/AgCl).

#### FIGURE AND TABLE LEGENDS:

**Figure 1. Macrotube and macrobeam synthesis scheme.** (A) Addition of  $[\text{PtCl}_4]^{2-}$  and  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  (B)  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  with  $[\text{PdCl}_4]^{2-}$  and/or  $[\text{PtCl}_4]^{2-}$ , or (C)  $[\text{Cu}(\text{NH}_3)_4]^{2+}$  with  $[\text{PtCl}_4]^{2-}$  and  $[\text{Pt}(\text{NH}_3)_4]^{2+}$  results in the formation of insoluble salt needles through linear stacking of oppositely charged square planar ions. Electrochemical reduction of salt needle templates forms either a porous macrotube or macrobeam with a square cross section. Representative polarized optical microscopy images of salt crystal templates are shown for each salt template type. Adapted from references 29, 31, and 32 with permission.

**Figure 2. Scanning electron micrographs of platinum macrotubes.** Adapted from reference 29 with permission.

**Figure 3. Scanning electron micrographs of platinum-palladium macrobeams.** Macrobeams formed from  $\text{Pt}^{2+}:\text{Pd}^{2+}:\text{Pt}^{2-}$  salt-template ratios of (A)–(B) 1:1:0 (C)–(D) 2:1:1, and (E)–(F) 3:1:2, with 100 mM salt solutions and reduced in 100 mM  $\text{NaBH}_4$ . Adapted from reference 31 with permission.

**Figure 4. SEM images of copper-platinum macrotubes reduced with DMAB.** Macrotubes formed from  $\text{Pt}^{2+}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salt-template ratios of (A)–(C) 1:0:1 (D)–(F) 3:1:2 (G)–(I) 2:1:1, and (J)–(L) 1:1:0. Adapted from reference 32 with permission.

**Figure 5. X-ray diffraction spectra** for (A) platinum macrotubes (B) platinum-palladium macrobeams (C) copper-platinum macrotubes reduced with DMAB, and (D) copper-platinum macrotubes reduced with  $\text{NaBH}_4$ . (B)  $\text{Pt}^{2+}:\text{Pd}^{2+}:\text{Pt}^{2-}$  and (C)–(D)  $\text{Pt}^{2+}:\text{Pt}^{2+}:\text{Cu}^{2+}$  salt-template ratios are indicated on the spectra. Adapted from references 29, 31, 32 with permission.

**Figure 6. X-ray photoelectron spectra** for (A) platinum macrotubes (B)–(C) platinum-palladium macrobeams; (B) Pt 4d<sub>5/2</sub>, Pt 4d<sub>3/2</sub>, Pd 3d<sub>3/2</sub>, and Pd 3d<sub>5/2</sub> peaks; (C) normalized Pt 4f<sub>7/2</sub> and Pt 4f<sub>5/2</sub> peaks. (D)–(E) copper-platinum macrotubes reduced with DMAB; (D) normalized Pt 4f<sub>5/2</sub> and Pt 4f<sub>7/2</sub>; (E) Cu 2p<sub>1/2</sub> and Cu 2p<sub>3/2</sub> peaks. Adapted from references 29, 31, 32 with permission.

**Figure 7. Electrochemical characterization of platinum macrotubes synthesized from 100 mM Magnus' salts.** (A) Platinum macrotube pressed film. (B) Electrochemical impedance spectroscopy (EIS) in 0.5 M KCl electrolyte at frequency range of 100 kHz to 1 mHz; (inset) high frequency EIS spectrum (C) Specific capacitance ( $C_{sp}$ ) in 0.5 M KCl electrolyte determined from EIS in (b). (D) CV in 0.5 M  $\text{H}_2\text{SO}_4$  at scan rates of 10, 5, 1, and 0.5 mVs<sup>-1</sup>. (E) CV in 0.5 M  $\text{H}_2\text{SO}_4$  from (D) at a scan rate of 1 mVs<sup>-1</sup>. Adapted from reference 29 with permission.

**Table 1.** Atomic ratio composition of Pt–Pd macrobeams synthesized from  $\text{Pt}^{2+}:\text{Pd}^{2+}:\text{Pt}^{2-}$  salt

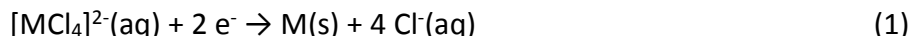
ratios of 1:1:0, 2:1:1, and 3:1:2 determined from salt stoichiometry, energy-dispersive x-ray spectroscopy (EDS), and x-ray photoelectron spectroscopy (XPS). Adapted from reference 31 with permission.

**Table 2.** Atomic composition of Pt–Cu macrotubes and macrobeams reduced with NaBH<sub>4</sub> and DMAB, respectively. Adapted from reference 32 with permission.

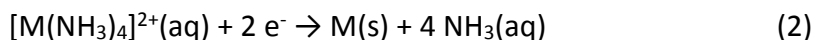
## DISCUSSION:

This synthesis method demonstrates a simple, relatively fast approach to achieve high-surface area platinum-based macrotubes and macrobeams with tunable nanostructure and elemental composition that may be pressed into free-standing films with no required binding materials. The use of Magnus' salt derivatives as high aspect ratio needle shaped templates provides the means to control resulting metal composition through salt-template stoichiometry, and when combined with choice of reducing agent, control over the nanostructure of the macrotube and macrobeam porous sidewalls and cross sectional structure. The synthesis method may be varied by changing the salt ratios used to form the templates: Pt<sup>2+</sup>:Pt<sup>2-</sup>, Pt<sup>2+</sup>:Pd<sup>2-</sup>:Pt<sup>2-</sup>, and Pt<sup>2-</sup>:Pt<sup>2+</sup>:Cu<sup>2+</sup>. Critical to this method is the formation of salt needle templates resulting from the addition of noble metal square planar cation and anions. Salt formation is found to be sensitive to water impurities and pH requiring the use of deionized water. It is also critical to ensure that electrochemical reduction is conducted within a fume hood with reaction tubes uncapped to prevent overpressure from the vigorous hydrogen evolution that results.

With this method, the reduction of [MCl<sub>4</sub>]<sup>2-</sup> to M<sup>0</sup>, shown in Equation 1, releases four Cl<sup>-</sup> ions into solution near the salt template surface where M is either Pt or Pd:



The charge balance for each [MCl<sub>4</sub>]<sup>2-</sup> ion is reduced; it is thought to be maintained by two [M(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> ions dissolving into solution. Four neutral ammonia molecules are released through the reduction of [M(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> to M<sup>0</sup> as shown in Equation 2:



The interaction of weakly basic ammonia with water is charge neutral to form NH<sub>4</sub><sup>+</sup> and OH<sup>-</sup> ions. The proposed reduction-dissolution action and nanoparticle surface free energy minimization likely contributes to the porous macrotube and macrobeam structures observed in **Figures 2, 3, and 4**<sup>29,31,32</sup>. Given this proposed mechanism, the salt-templates are in part self-sacrificial given the conversion of some of the salt to the metal phase with the remainder of the salt leaving the template with open pores remaining in its place.

One obvious limitation to the generalizability of this approach is the small number of oppositely charged square planar metal ion combinations available. These are generally limited to coordination complexes of platinum, palladium, copper, gold, and nickel, for example: [PtCl<sub>4</sub>]<sup>2-</sup>, [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [Cu(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup>, [AuCl<sub>4</sub>]<sup>-</sup>, and [Ni(CN)<sub>4</sub>]<sup>2-</sup>. The use of [Ni(CN)<sub>4</sub>]<sup>2-</sup>, while compelling as a

low-cost transition metal that might be used in combination with platinum, palladium, and copper square planar cations, presents a significant safety issue with the liberation of CN<sup>-</sup> ions during electrochemical reduction in combination with hydrogen gas evolution. Other platinum and palladium coordination complexes have been demonstrated to precipitate insoluble salts<sup>35-37</sup>. The formation of high aspect ratio salt needles is believed to depend on the relative matching of cation and anion size, with greater mismatch leading to less product yield.

The hand-pressing of free-standing films works best with platinum macrotubes likely due to the entanglement of the high aspect ratio structures conforming to the salt-templates. These films are robust to mechanical manipulation with tweezers remaining intact between transfer steps from pressing to placement in an electrochemical vial; however, films will fracture with severe bending. Platinum-palladium microbeam pressed films are not as mechanically robust as platinum macrotubes, likely due to the smaller feature size of the macrobeams. Copper-platinum pressed films are the least mechanically durable of the metal combinations described in this method, though they are stable enough to transfer to electrochemical vials for impedance spectroscopy and cyclic voltammetry. Depending on practical device applications, a minimum of polymeric binder may be used to enhance the structural integrity of the copper-platinum films.

The primary advantage of this method is the simplicity, relative speed, metal composition control, and nanostructure of the macrotube and macrobeam synthesis, as well as the ability to press the synthesis products into free-standing films. With nanoscale feature sizes as small as 4-5 nm for platinum macrotubes, this synthesis method is comparable to preformed nanoparticle sol-gel methods to form noble metal aerogels but without the need for supercritical drying. Platinum-palladium and copper-platinum macrobeams and macrotubes, though, have a slightly larger nanostructure feature size ranging up to 50 nm. The larger feature size is partially offset by the ability to incorporate low-cost copper into the nanostructure and tune elemental composition. This method is envisioned to be scalable to any reaction volume from low milliliter to 10s of liters if required.

While the available square planar metal ions are limited for the formation of salt needles comprised of metallic cations and anions, the use of insoluble metal salts may be generalizable to salts where only one ion is metallic. This salt-templating synthesis method might create a much larger range of achievable metal, metal oxide, alloy, and multi-metallic nanostructures.

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#### **DISCLOSURES:**

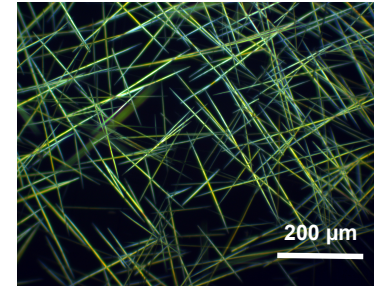
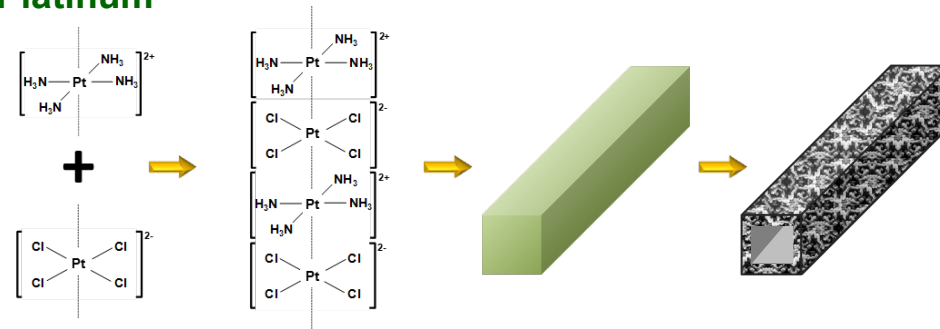
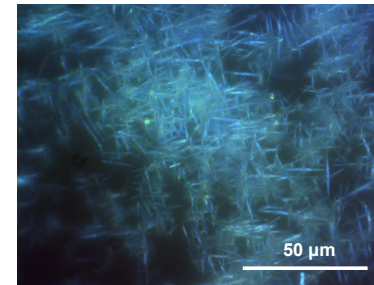
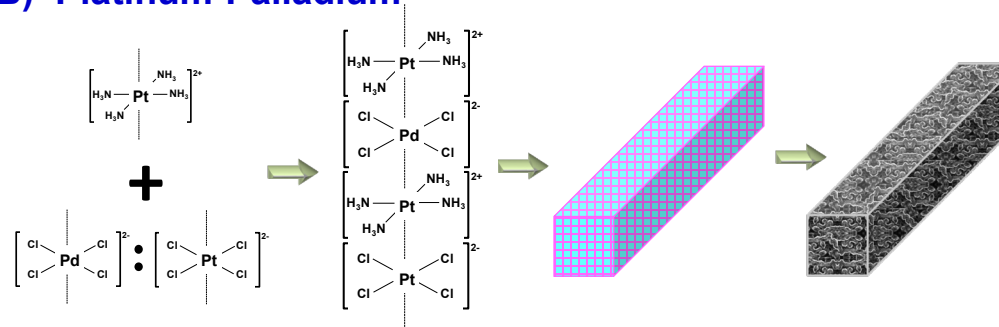
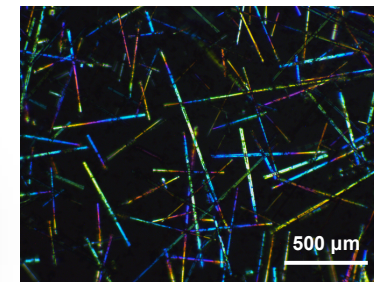
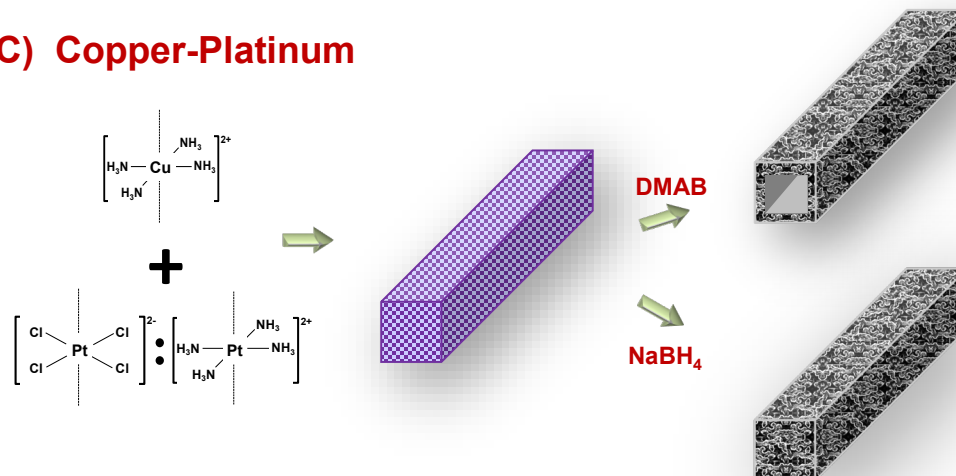
The authors have nothing to disclose.

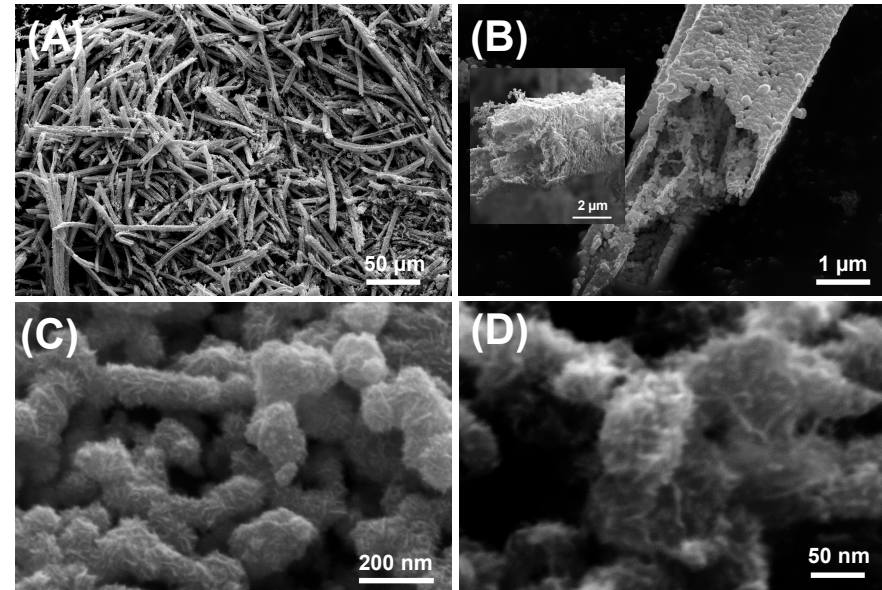
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Figure 1

[Click here to access/download;Figure;Figure 1.pdf](#)**(A) Platinum****(B) Platinum-Palladium****(C) Copper-Platinum**





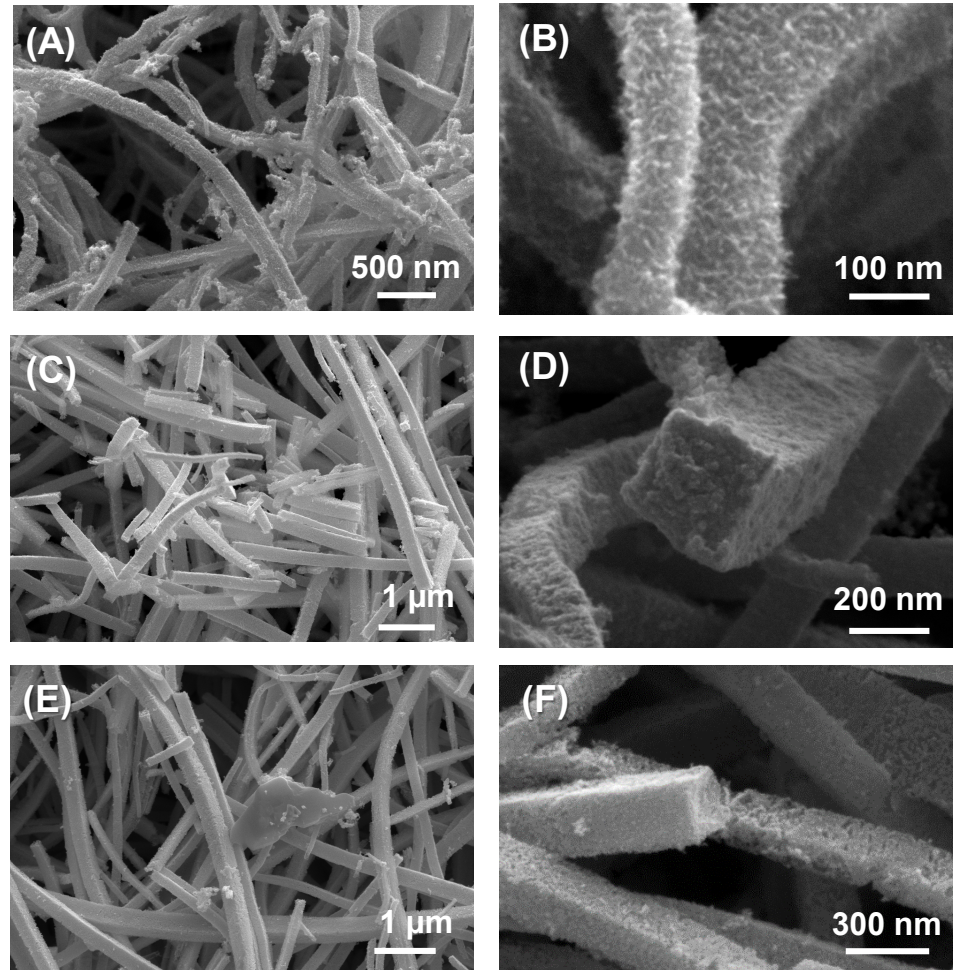


Figure 4

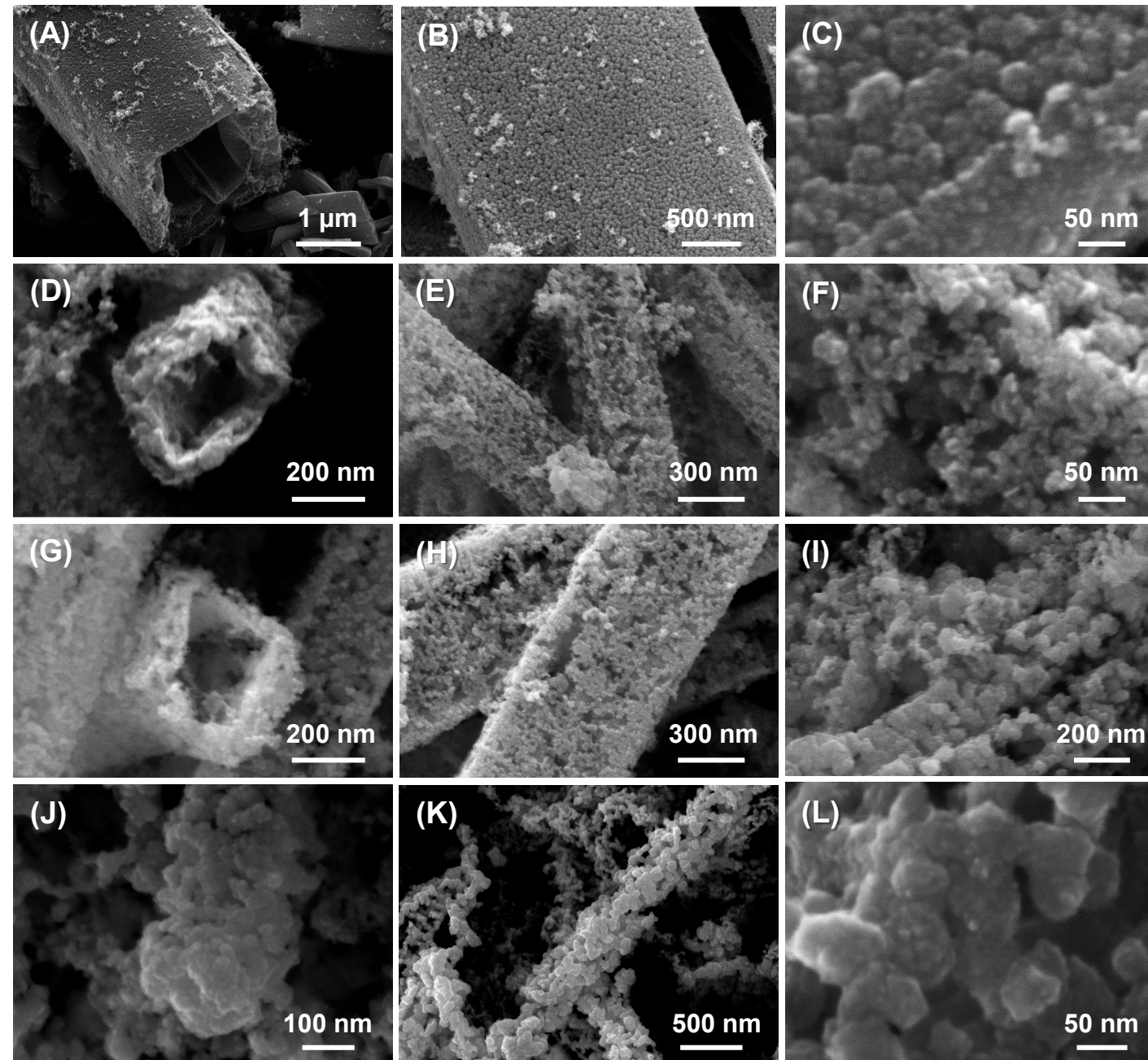


Figure 5

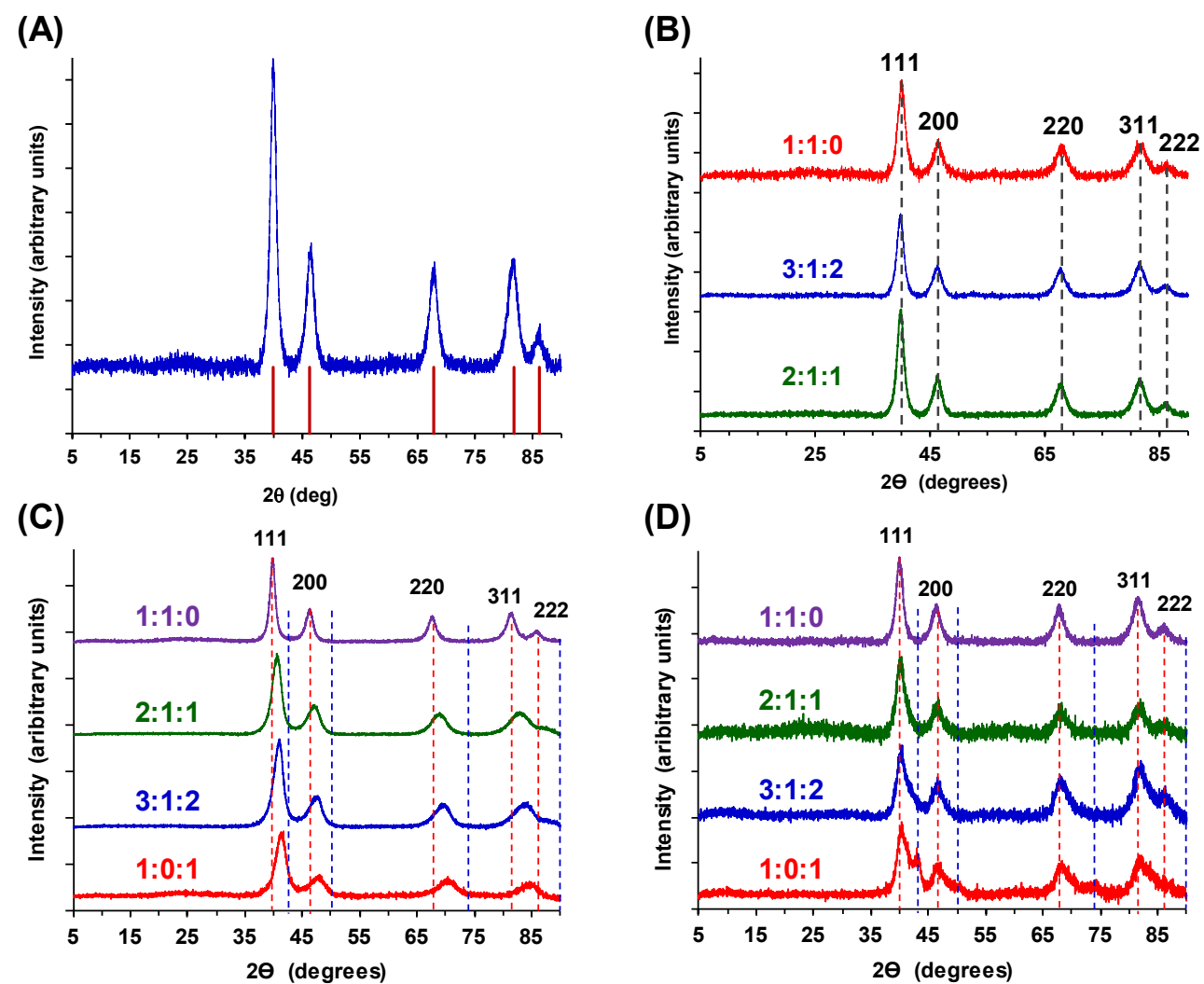




Figure 6

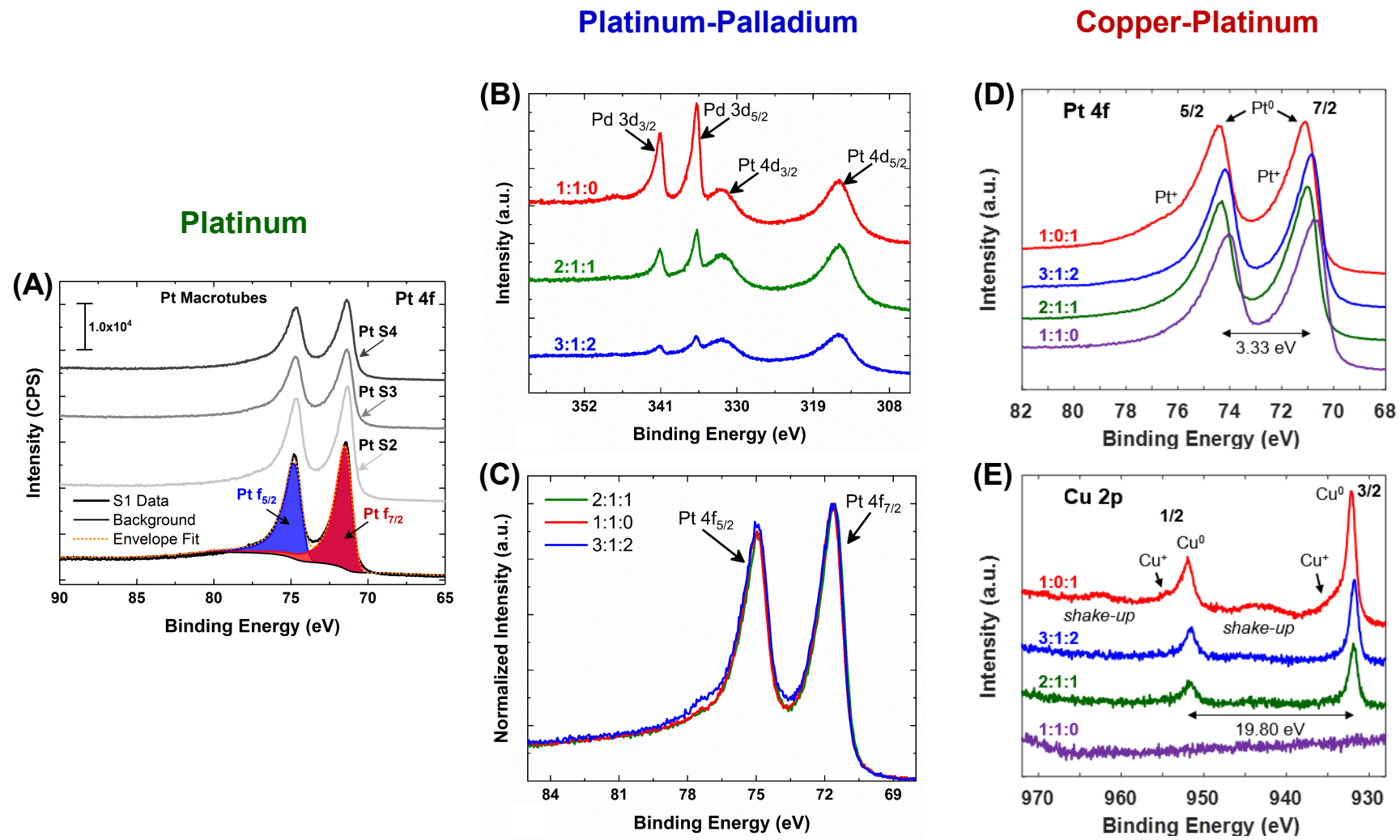
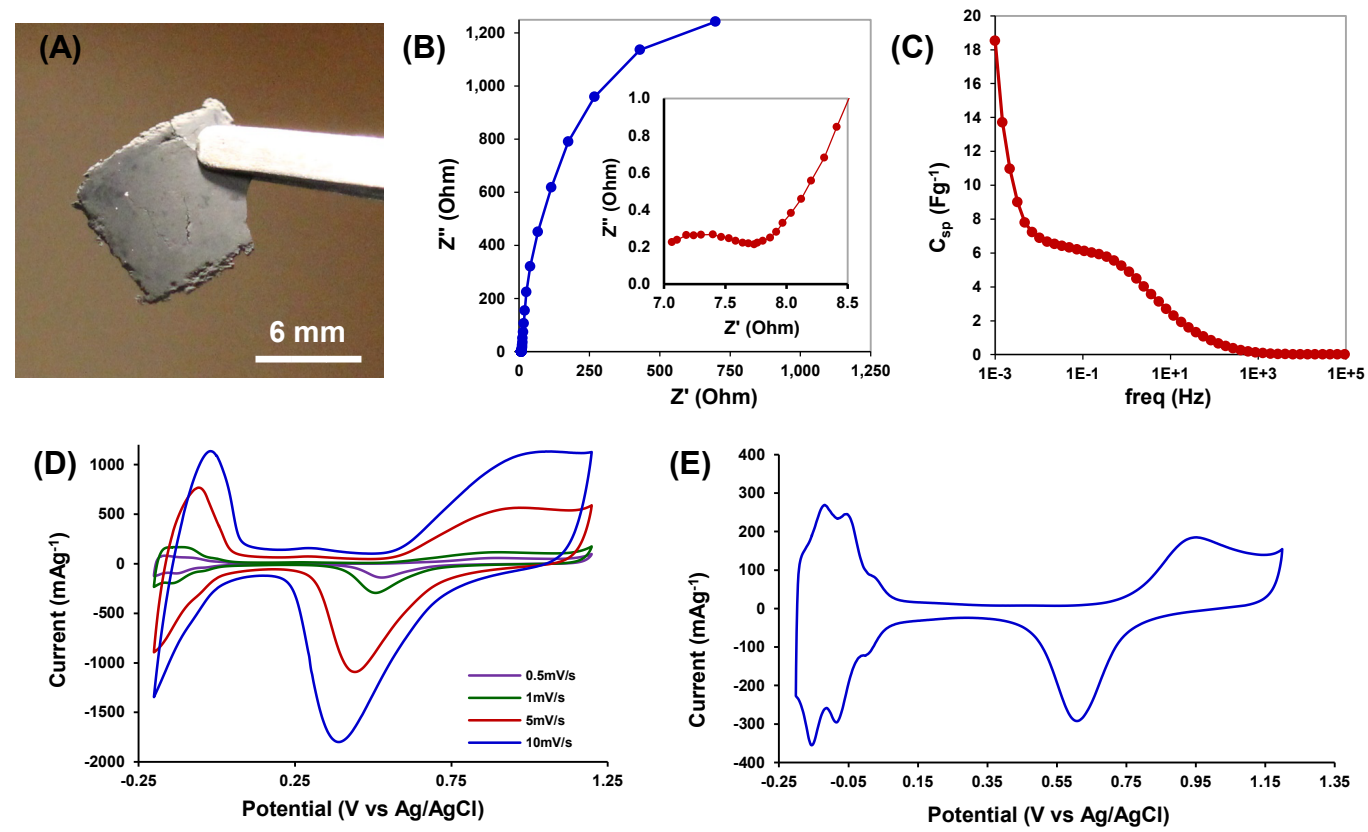


Figure 7



<b>Pt<sup>2+</sup> : Pd<sup>2-</sup> : Pt<sup>2-</sup></b>	<b>Stoic. Pt:Pd</b>	<b>EDS Pt:Pd</b>	<b>XPS Pt:Pd</b>
<b>1:1:0</b>	1:1	1.12:1	1.89:1
<b>2:1:1</b>	3:1	3.50:1	6.45:1
<b>3:1:2</b>	5:1	6.35:1	11.7:1

		Pt <sup>2-</sup> :Pt <sup>2+</sup> :Cu <sup>2+</sup>	Stoic. Pt:Cu	EDS Pt:Cu	XPS Pt:Cu
		1:0:1	1:1	0.5:1	0.92:1
DMAB	NaBH <sub>4</sub>	3:1:2	2:1	1.3:1	3.1:1
		2:1:1	3:1	2.5:1	4.0:1
		1:1:0	1:0	1:00	1.0:0
		1:0:1	1:1	0.7:1	2.2:1
		3:1:2	2:1	1.5:1	5.8:1
		2:1:1	3:1	2.1:1	7.9:1
		1:1:0	1:0	1:00	1.0:0

Name of Material/ Equipment	Company	Catalog Number	Comments/Description
50 mL Conical Tubes	Corning Costar Corp.	430290	
Ag/AgCl Reference Electrode	BASi	MF-2052	
Cu(NH <sub>3</sub> ) <sub>4</sub> SO <sub>4</sub> •H <sub>2</sub> O	Sigma-Aldrich	10380-29-7	
dimethylamine borane (DMAB)	Sigma-Aldrich	74-94-2	
K <sub>2</sub> PtCl <sub>4</sub>	Sigma-Aldrich	10025-99-7	
	Tober Chemical		
Miccrostop Lacquer	Division	NA	
Na <sub>2</sub> PdCl <sub>4</sub>	Sigma-Aldrich	13820-40-1	
NaBH <sub>4</sub>	Sigma-Aldrich	16940-66-2	
Polarized Optical Microscope	AmScope	PZ300JC	
Potentiostat	Biologic-USA	VMP-3	Electrochemical analysis-EIS, CV
Pt wire electrode	BASi	MF-4130	
Pt(NH <sub>3</sub> ) <sub>4</sub> Cl <sub>2</sub> •H <sub>2</sub> O	Sigma-Aldrich	13933-31-8	
Scanning Electron Microscope	FEI	Helios 600 Vari-Mix™	EDS performed with this SEM
Shelf Rocker	Thermo Scientific	Platform Rocker	
Snap Cap Microcentrifuge Tubes, 1.7 mL	Cole Parmer	UX-06333-60	
X-ray diffractometer	PanAlytical	Empyrean	X-ray diffractometry
	ULVAC PHI - Physical		
X-ray photoelectron spectrometer	Electronics	VersaProbe III	





DEPARTMENT OF THE ARMY  
UNITED STATES MILITARY ACADEMY  
WEST POINT, NY 10996

April 14, 2020

Dear Sir/Ma'am,

We have addressed the editorial and reviewer comments for our manuscript JoVE61395 entitled "Salt-Templated Synthesis Method for Porous Platinum-based Macrobeams and Macrotubes" by F. John Burpo, Anchor R. Losch, Enoch A. Nagelli, *et al.* Our responses to the comments are indicated in red font below.

We appreciate the consideration of our work and the opportunity to address the concerns identified during the review, as well as your patience during these extraordinary times. Please let us know if there is anything else needed.

Respectfully,

A handwritten signature in black ink, appearing to read "F. John Burpo", is written over a light gray rectangular background.

F. John Burpo, Sc.D.  
Colonel, U.S. Army  
Professor and Head, Department of  
Chemistry & Life Science

## Editorial comments:

Changes to be made by the Author(s):

1. Please take this opportunity to thoroughly proofread the manuscript to ensure that there are no spelling or grammar issues. The JoVE editor will not copy-edit your manuscript and any errors in the submitted revision may be present in the published version.

Complete.

2. Please sort the Materials Table alphabetically by the name of the material.

Complete.

3. Please highlight 2.75 pages or less of the Protocol (including headings and spacing) that identifies the essential steps of the protocol for the video, i.e., the steps that should be visualized to tell the most cohesive story of the Protocol. Remember that non-highlighted Protocol steps will remain in the manuscript, and therefore will still be available to the reader.

Yellow highlighted sections were reduced based on the guidance in #4 below. The current highlighted sections sum to approximately 2.75 pages.

4. The solution preparation steps can be excluded from the filming for example.

Yellow highlights were removed for solution preparation steps (Step 1.1 and Step 2.1).

5. Please ensure that the highlighted steps form a cohesive narrative with a logical flow from one highlighted step to the next. Please highlight complete sentences (not parts of sentences). Please ensure that the highlighted part of the step includes at least one action that is written in imperative tense.

Verified.

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Completed.

## Reviewers' comments:

### *Reviewer #1:*

We appreciate Reviewer #1's comments to help clarify the protocol details and presentation.

#### *Manuscript Summary:*

The paper describes a simple and fast method for making platinum-based macrotubes and macrobeams. The manuscript is well written and clear. I recommend that it be published in Jove so long as the minor concerns listed below are addressed.

#### *Major Concerns:*

n/a

#### *Minor Concerns:*

The comments below are intended to improve the methods description.

Line 37: Please recommend a container (beaker, tube??)

Line 37 is an author email address. If the comment was to add a container recommendation to the initial safety Note on Line 137, our intent was to provide a general safety notice about the gas evolution associated with any "reaction tube" with specific tube types identified/recommended in the various steps later in the protocol.

Line 165 (and other places): Please be more specific as to what is meant by "forcefully pipette" (if possible) or explain why it must be forceful.

To clarify the practical meaning of "forceful pipetting," the following sentence was added after the first "forceful pipetting" step in Step 1.2.1: "Forceful pipetting is dispensing the full reagent volume within 1 second to ensure rapid mixing of chemicals within microfuge tubes."

Lines 214-216 (Instruction 1.4.4): I am confused. Isn't this the same as 1.2.1. The chemicals listed are different.

Step 1.4.4 results in the formation of the same salt template as in Step 1.2.1, however, the salts from 1.2.1 will later be reduced with  $\text{NaBH}_4$  in Step 2.2.1, and the salts from 1.4.4 will be reduced with DMAB in Step 2.2.2.

Step 1.4.4. incorrectly listed  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  for both reagents to be combined. The authors appreciate Reviewer #1 identifying this error. The revised step now reads:

"1.4.4. To prepare the salt ratio 1:1:0, pipette 0.5 mL of 100 mM  $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$  into a microfuge tube. Forcefully pipette 0.5 mL of 100 mM  $\text{K}_2\text{PtCl}_4$  into the microfuge tube for a total of 1 mL salt needle template solution."

Line 220: I like the inclusion of information about color changes - it will be very helpful to someone trying to do this.

We hope the included Notes regarding salt colors will be visually communicated well in the accompanying video.

Lines 245-6: Consider moving the Note to the start of the section (i.e. by line 235).

Thank you for this suggestion. The Note was moved to Line 235 and we believe it will be more helpful at the beginning of the protocol Step.

Step 2.2.1: The instructions are a bit unclear. How much should be pipetted into each tube (all)? I suggest something like "Pipette the solution of 1.2.1 into conical tube 1, pipette the solution of 1.3.1 into conical tube 2...."

Step 2.2.1 was changed, with additions in bold, to read: "2.2.1. In a fume hood, pipette **the entire 1 mL volume of** each of the salt template solutions from Steps 1.2 and 1.3 into each of 4, 50 mL conical tubes of 0.1 M NaBH<sub>4</sub> reducing agent. Allow the chemical reduction to continue for 24 hours with the cap off the tube." Similar verbiage was added to Step 2.2.2.

Given the number of samples and sample nomenclature designations, e.g. Pt<sup>2+</sup>:Pd<sup>2+</sup>:Pt<sup>2+</sup>, 1:0:1, we recommend avoiding additional conical tube designations.

The instructions also indicate to leave the caps off. Was anything used to cover (i.e. loose parafilm?)

Given the first Note recommendation to perform all reactions in a fume hood, we were not overly concerned about dust/contamination, but have occasionally put loose parafilm or foil over the tubes given conditions in the lab. To address this issue, the following line was added to the Note after Step 2.2.2:

"Loose parafilm or foil may be placed over the tubes if dust contamination is a concern."

Steps 2.3.2 & 2.3.2 - cover or no cover?

Steps 2.3.2 and 2.3.3 have an added phrase "with tube caps secured" and now read as:

"2.3.2. Pour each of the precipitates into new 50 mL conical tubes. The use of a spatula may be required to dislodge sample adhering to the tube sidewalls. Fill each of the new tubes with 50 mL de-ionized water and place on a rocker **with tube caps secured** at a low setting for 24 hours."

Line 295. Please indicate approximate height that should results.

Step 3.1.2 now reads as, "3.1.2. Using a spatula, gently transfer the precipitate material to a glass slide. Using a spatula, consolidate the sample into a pile with uniform height **of approximately 0.5 mm.**"

Step 3.1.3: Should the glass slides be covered with anything?

As long as there are no air currents and significant concern for dust contamination, there is no need to cover the slides.

**Reviewer #2:**

We appreciate Reviewer #2's comments particularly regarding consideration of the formation mechanism and terminology.

The manuscript described and general method to prepare micro-sized tubes, and I strongly appreciate the clearly description of safety CAUTIONs and notes. I prefer to accept this manuscript after considering the following comments:

1, In my opinion the formation process is a Self-sacrificial template process. While salt-template will mis-lead me to use salt as a solid template, which did not involve in the reactions. like the previous reports: Nature Communication, 2014, 5, 3605; Chemical Communications, 2018, 54, 25, 3158-3161.

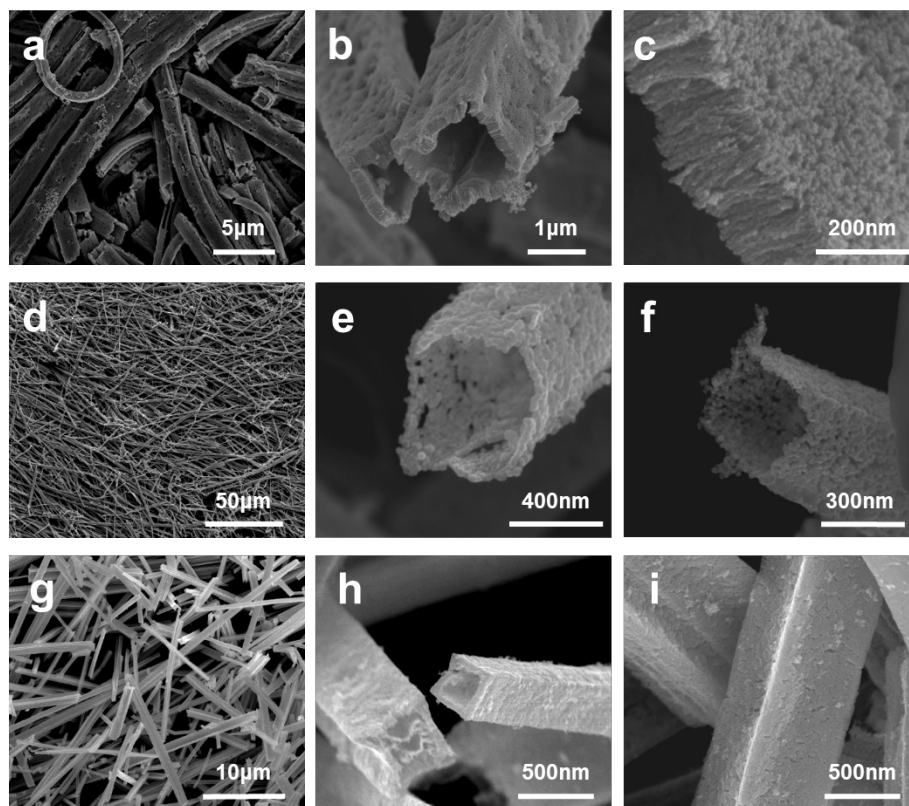
The authors thank Reviewer #2 for the nuanced insight that the salt-template needles are self-sacrificial in that the template is partially metallized, while the remainder of the template is hollowed/sacrificed to become the cavity and pore network. To convey this nuance, the following verbiage was added as Lines 518-520 in the Discussion section:

“Given this proposed mechanism, the salt-templates are in part self-sacrificial given the conversion of some of the salt to the metal phase with the remainder of the salt leaving the template with open pores remaining in its place.”

2, The formation process of hollow tube should be studied. And I propose the formation of tube is based on a Kirkendall process, like the conversion from CuOx to Cu<sub>7</sub>S<sub>4</sub>, Cu<sub>2-x</sub>Se, (Journal of Materials Chemistry A, 2016, 4, 13, 4790-4796. Journal of Power Sources, 2015, 299, 212-220. Chemistry - A European Journal, 2014, 20, 42, 13576-13582. Nano Energy, 2015, 12, 0, 186-196.)

Our group has previously considered the possibility of the Kirkendall effect as a possible mechanism of macrotube formation and we appreciate Reviewer #2's insight and suggestion. While this manuscript describes the synthesis of multi-metallic Pt-Pd and Cu-Pt materials, it also describes a Pt-only material based on our first report of salt-templating: Burpo, F. J. et al. Salt-Templated Hierarchically Porous Platinum Macrotube Synthesis. *ChemistrySelect*. 3 (16), 4542-4546, (2018). Given the Pt macrotube formation from a monometallic metal salt template, the Kirkendall effect does not seem to be the likely mechanism given the absence of a second metal with dissimilar diffusivities leading to voids in the crystal structure for pore formation.

We have also observed tube formation for a single Pd phase using Vauquelin Salt templates, ie [PdCl<sub>4</sub>]<sup>2-</sup> and [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> (this work is prepared for submission and a draft figure with SEM images is copied below showing tube formation with different reducing agents. Again, tube formation is observed in the absence of a second diffusing metal).



**Figure 3.** Scanning electron microscope images of palladium nanotube morphology dependence on reducing agent used. (a), (b), (c) 50 mM Pd-Pd salt needles reduced with 0.1 M dimethylamine borane. 100mM Pd-Pd salt needles were reduced with the following reducing agents: (d), (e), (f) 0.1 M sodium hypophosphite. (g), (h), (i) 0.2 M chromium (II) chloride.

3, I strongly suggest to identify the composition of alloys by ICP method. Because eds and XPS is semiquantitative

The authors agree that EDS and XPS are semi-quantitative techniques and that ICP would provide an additional quantitative assessment of the metal composition of the macrobeams and macrotubes. EDS determined metal composition has correlated well with the salt-template stoichiometries for the following studies that are the basis of this protocol manuscript:

- Burpo, F., Nagelli, E., Morris, L., Woronowicz, K. & Mitropoulos, A. Salt-Mediated Au-Cu Nanofoam and Au-Cu-Pd Porous Macrobeam Synthesis. *Molecules*. **23** (7), 1701, (2018).  
 Burpo, F. J. *et al.* Salt-templated platinum–palladium porous macrobeam synthesis. *MRS Communications*. **9** (1), 280-287, (2019).  
 Burpo, F. J. *et al.* Salt-Templated Platinum-Copper Porous Macrobeams for Ethanol Oxidation. *Catalysts*. **9** (8), 662, (2019).

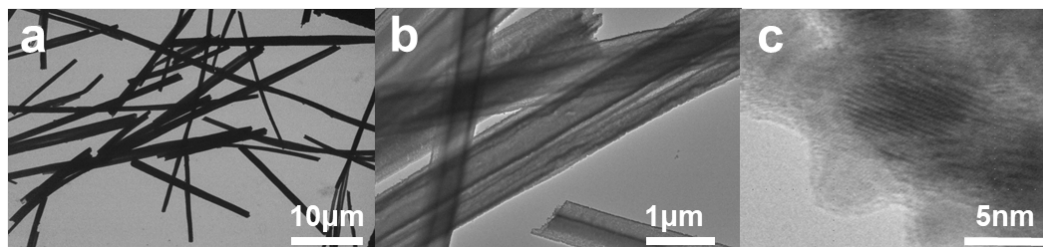
In a comparison study between EDS and ICP for suspended particulate matter, EDS and ICP median metal concentration values were similar and accurate (S. M. Haley, A. D. Tappin, P. R. Bond, M. F. Fitzsimons. A comparison of SEM-EDS with ICP-AES for the quantitative elemental determination of estuarine particles. *Environ Chem Lett* 4, 235–238 (2006)). In another study that compared the ICP and EDS values for determining the Cu-Sn metal composition in bronze, the ICP and EDS values were also found to be very similar.

While conducting ICP would more quantitatively assess the bi-metallic macrotube and macrobeam compositions, given the salt stoichiometry to EDS mass ratio correlations of our previous salt-

templating work, the correlations between ICP and EDS in other studies, and the indefinite lack of access to our university laboratory during the COVID-19 pandemic, we respectfully suggest that ICP data not be required for this synthesis protocol.

4. The surface area and TEM images of products are request.

TEM images were taken for our forthcoming work on Vauquelin Salt templated Pd macrotubes as seen in the draft figure below. Our experience is that SEM is a more effective imaging technique to characterize the surface and pore structure than TEM for which contrast between nanoparticles and thicker side walls is challenging.



**Figure 5.** High resolution transmission electron microscope (HRTEM) images of 100 mM Pd-Pd palladium salts reduced with 0.2 M  $\text{CrCl}_2$ . (a) A straight tube morphology is seen at the multi-micron length scale. (b) At the micron scale the Pd nanotubes present smooth walls. (c) Higher magnification indicates nanocrystals with varied orientations. The lattice constant for fcc Pd is  $3.89\text{\AA}$  and the measured lattice spacing is approximately  $3.9\text{\AA}$ . The  $d_{111}$  spacing for fcc Pd is  $2.25\text{\AA}$  and the measurement is approximately  $2.3\text{\AA}$ .

Specific surface areas were estimated via specific capacitance from electrochemical impedance spectroscopy (EIS) and provided for platinum macrotubes in Lines 436-437: “The estimated  $C_{\text{sp}}$  is  $18.5\text{ Fg}^{-1}$  with a corresponding solvent accessible specific surface area of  $61.7\text{ m}^2\text{g}^{-1}$ .” Nitrogen gas adsorption-desorption and BET analysis would offer a complementary technique, but would be extremely expensive to synthesize the requisite mass of Pt and Pd materials, in addition to the current lack of lab access in American universities due to COVID-19.



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