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

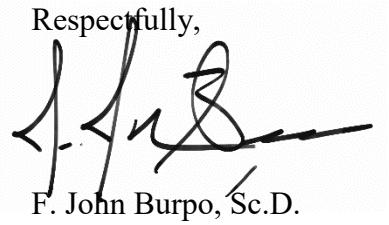
April 14, 2020

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,



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

6. Please obtain explicit copyright permission to reuse any figures from a previous publication. Explicit permission can be expressed in the form of a letter from the editor or a link to the editorial policy that allows re-prints. Please upload this information as a .doc or .docx file to your Editorial Manager account. The Figure must be cited appropriately in the Figure Legend, i.e. “This figure has been modified from [citation].”

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 $NaBH_4$ 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 $Pt(NH_3)_4Cl_2 \cdot H_2O$ 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 $Pt(NH_3)_4Cl_2 \cdot H_2O$ into a microfuge tube. Forcefully pipette 0.5 mL of 100 mM K_2PtCl_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 so 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 $NaBH_4$ 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^{2+}:Pd^{2-}:Pt^{2-}, 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 microsized 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 kirkendal process, like the conversion from CuOx to Cu7S4, Cu2-xSe,(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 $[PdCl_4]^{2-}$ and $[Pd(NH_3)_4]^{2+}$ (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).

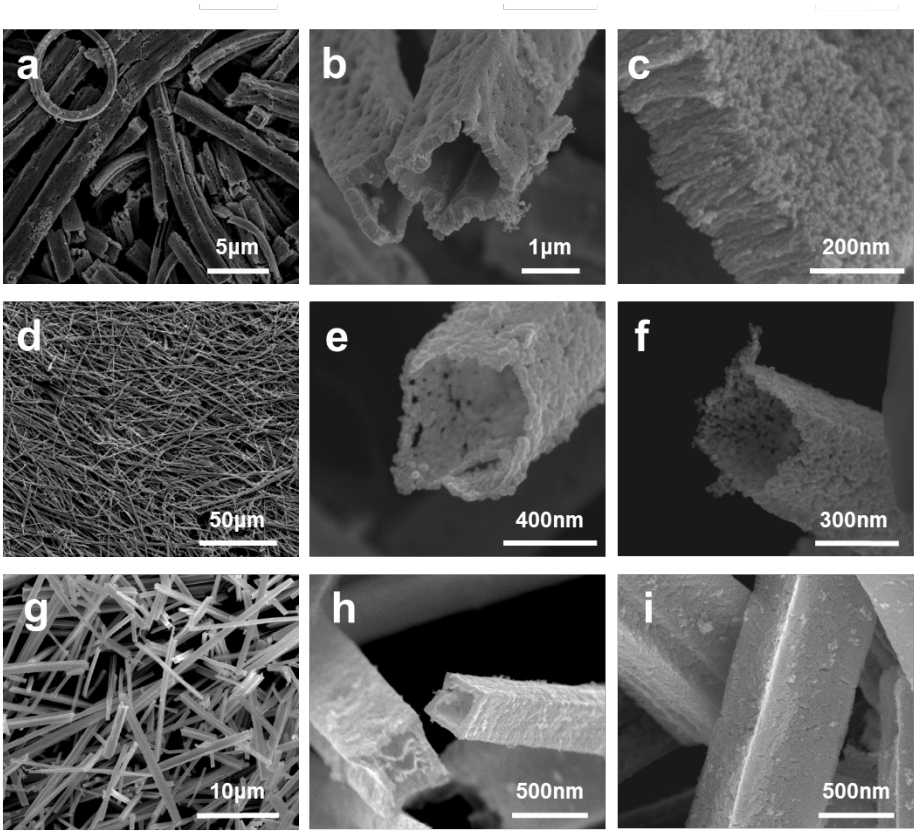

Figure 3. Scanning electron microscope images of palladium nanotube morphology dependence on reducing agent used. (a), (b), (c) 50 mM Pd-Pd salt needles reduced with 0.1 M dimethylamine borane. 100mM Pd-Pd salt needles were reduced with the following reducing agents: (d), (e), (f) 0.1 M sodium hypophosphite.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

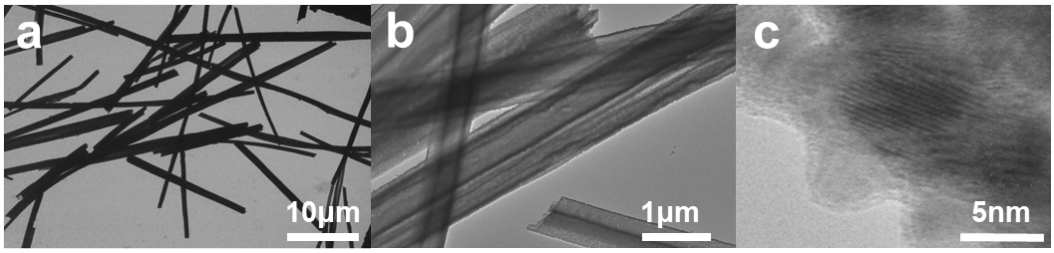

Figure 5. High resolution transmission electron microscope (HRTEM) images of 100 mM Pd-Pd palladium salts reduced with 0.2 M $CrCl_2$. (a) A straight tube morphology is seen at the multi-micron length scale. (b) At the micron scale the Pd nanotubes present smooth walls. (c) Higher magnification indicates nanocrystals with varied orientations. The lattice constant for fcc Pd is 3.89Å and the measured lattice spacing is approximately 3.9Å. The d_{111} spacing for fcc Pd is 2.25Å and the measurement is approximately 2.3Å.

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_{sp} is 18.5 Fg^{-1} with a corresponding solvent accessible specific surface area of 61.7 m^2g^{-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.