## Salt-templated metal and metal oxide porous materials

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Pure metal, multi-metallic and alloy nanomaterials enable a broad range of catalytic applications with high surface area and tunable reaction specificity through the variation of metal composition. Synthesizing these materials as three-dimensional porous nanostructures enables control of surface area, pore size and mass transfer properties, electronic conductivity, and ultimately device integration. Discrete and aggregated nanoparticles offer tremendous design flexibility, yet methods to assemble them into extended 3-dimensional structures suffer from several limitations, especially aggregation and diffusion times. Insoluble salts offer a template approach to synthesize of a range of porous noble and transition metal structures and monoliths. Magnus and Vauquelin salt needles formed from the combination of oppositely charged square planar ions serve as templates that are chemically reduced. This approach has been demonstrated for Pt, Pd, Pt-Pd, Cu-Pt, Au-Cu, and Au-Cu-Pd salts and resulting porous macrotubes and macrobeams 10's to 100's of micrometers long with square cross-sections ranging from approximately 100 nm to 3 µm.[1-4] Platinum macrotubes with square cross-section and porous sidewalls composed of fibril textured nanoparticles pressed into free-standing films exhibit a specific capacitance of 18.5 F/g and a solvent accessible specific surface area of 61.7 $m^2/g$.[1] Porous Pt-Pd macrobeams are templated from salt needles by combining $[PtCl_4]^{2-}$ and/or $[PdCl_4]^{2-}$ with $[Pt(NH_3)_4]^{2+}$ ions.[3] Porous side wall morphology and elemental composition was controlled with initial platinum to palladium salt ratios. Moreover, the use of salt templates was extended to sulfate and acetate salts to form to copper and nickel transition metal and metal oxide aerogels where the template salt anion influenced the metal oxide composition. Chloride salts of palladium and ruthenium were also demonstrated to form aerogels. The use of salt precursors is envisioned as a synthesis route to a wide range of metal and multi-metallic nanostructures for catalytic, energy storage, and sensing applications.

### References

1. Burpo, F.J., Nagelli, E., Winter, S., McClure, J., Bartolucci, S., Burns, A., O'Brien, S. "Salt-Templated Hierarchically Porous Platinum Macrotube Synthesis." *ChemistrySelect*. 2018, *3*, 4542-4546.
2. Burpo, F.J., Nagelli, E., Morris, L., Woronowicz, K., Mitropoulos, A. "Salt-Mediated Au-Cu Nanofoam and Au-Cu-Pd Porous Macrobeam Synthesis." *Molecules*. 2018, *23*, 1701-1715.
3. Burpo, F.J., Nagelli, E., Bartolucci, S., Mitropoulos, A., McClure, J., Baker, D., Losch, A., Chu, D. "Salt-Templated Platinum-Palladium Porous Macrobeam Synthesis." *MRS Communications,* 2019, 9(1), 280-287.
4. Burpo, F.J.*, Nagelli, E.A., Losch, A.R., Bui, J., Forcherio, G.T., Baker, D.R., McClure, J.P., Bartolucci, S.F., Chu, D.D. Salt-Templated Platinum-Copper Porous Macrobeams for Ethanol Oxidation. *Catalysts,* 2019, *9*(8), 662.