Microstructured Materials Synthesis
via Salt-assisted Ultrasonic Spray Pyrolysis

John W. Overcash Final Seminar June 20, 2013

Micro- and nanostructured materials are a very important part of today's technology due to their unique physical, optical, magnetic, and electrical properties. However, many methods of producing these materials require expensive precursors or templates and are complicated, multi-step procedures. Ultrasonic spray pyrolysis (USP) is an industrially-scalable technique that has been shown to yield relatively monodisperse sub-micron particles in a continuous process using inexpensive and, often, environmentally-friendly precursors.[1] The incorporation of an inert or reactive salt into the precursor solution allows for structural modification of the final product. Inert salts remain after solvent evaporation and provide a template for formation of the product.[2] The salt is then easily removed from the product by washing and can be reused. Reactive salts will decompose in the furnace creating gases which are known to increase the microporosity of products in USP.[3] This work shows the versatility of salt-assisted USP for making a wide variety of microstructured materials and highlights a few applications of the materials formed.

Salt-assisted USP has previously been used to make carbon spheres with diverse morphologies.[3a, 4] However, there is little predictive understanding of why one morphology is formed over another. This is especially true when dealing with salt mixtures. As a simple system, sucrose was pyrolyzed with different ratios of sodium nitrate and sodium chloride. It was shown that when a reactive salt ($NaNO_3$) is involved the salt ratio dictates the morphology of the product and that the furnace temperature (i.e., the phase of the salt solution) has little to no effect (Figure 1).

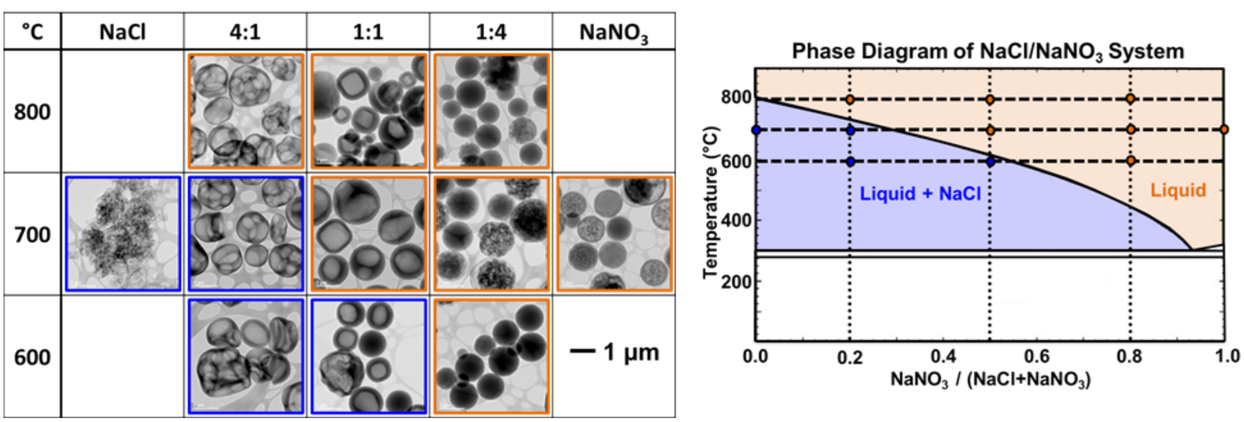

Figure 1: TEM images of porous carbon microspheres synthesized from sucrose at various temperatures using different ratios of NaCl and $NaNO_3$. The blue and orange outlines correspond to the blue and orange sections of the NaCl/$NaNO_3$ phase diagram.

With the addition of an iron precursor to the sucrose-based precursor solution, porous carbon microspheres containing iron oxide nanoparticles are made.[3b] These carbon microspheres are magnetic and have been shown to undergo magnetic heating. They are also capable of being loaded with and releasing ibuprofen, a cancer drug mimic. Creating a protein corona around the particles (as would occur in biological media or in vivo) slows the rate of release of the loaded drug. Thus, these spheres are promising candidates for use as multifunctional biomedical devices that incorporate hyperthermia therapy, controlled drug release, and biomedical imaging contrast.

Very high surface area iron oxide microspheres can also be produced easily from USP. The crystallinity of the final product can be controlled by adjusting the precursor solution. When aqueous Fe^{3+} salts react with a weak base (e.g., Na_2CO_3), a high molecular weight iron polymer that is stable in solution (so called Spiro-Saltman balls) is formed.[5] Using the Spiro-Saltman precursor, USP yields high surface area (~300 m^2/g) crystalline microspheres. If iron chloride is used in place of iron nitrate, hollow spheres are obtained which have a lower surface area (~100 m^2/g). Mixing different ratios of iron nitrate and iron chloride gives products with intermediate morphologies and surface areas (Figure 2). These iron oxide microspheres were tested as lithium-ion battery anodes.[6]

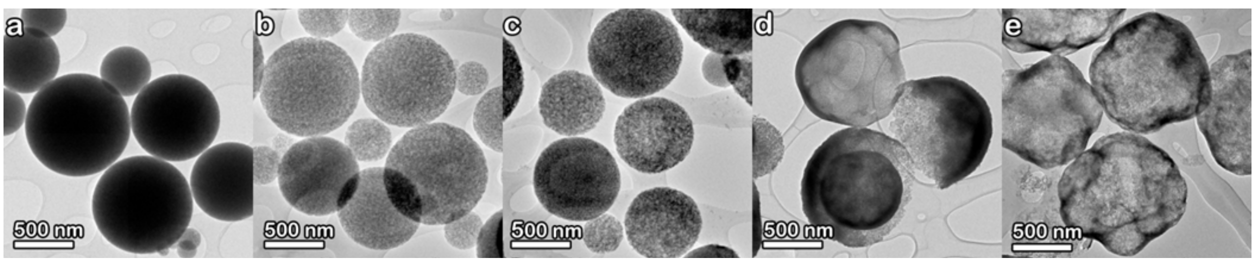

Figure 2: Porous iron oxide microspheres synthesized from Spiro-Saltman precursors using (a) $Fe(NO_3)_3$, (b) 4:1, (c) 1:1, (d) 1:4 $Fe(NO_3)_3/FeCl_3$, and (e) $FeCl_3$.

Finally, salt-assisted USP can be used to make roughened ZnO microspheres (Figure 2). Microspheres with varying degrees of roughness can be created by adjusting the amount of NaCl used as the salt-template. The size of the particles formed is also easily controlled by adjusting the concentration of the precursors in the precursor solution. By controlling both the size and the roughness of the ZnO particles formed, the hierarchical structure of a film of these particles can be controlled, which has consequences for the wetting properties of the film. Specifically, hierarchically structured films are known to stabilize the Cassie-Baxter state and encourage superhydrophobic (or superhygrophobic) behavior.[7]

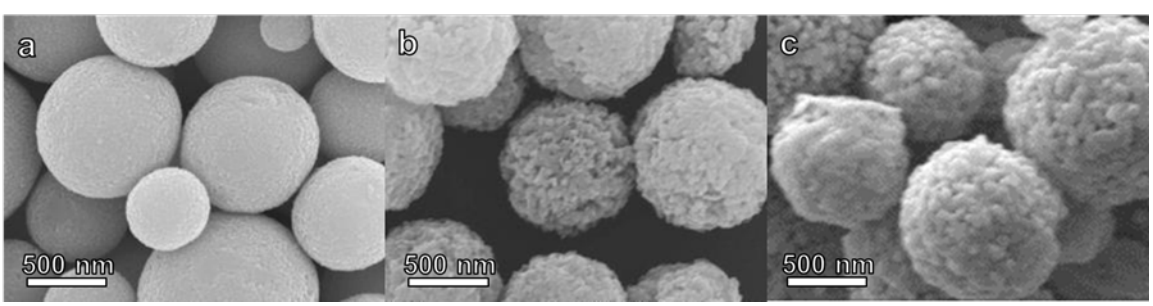

Figure 3: Zinc oxide microspheres from zinc oxide nanoparticles: (a) nanoparticles only, (b) nanoparticles with NaCl, washed, (c) nanoparticles with SiO_2 nanoparticles, etched.

Salt-assisted USP is a versatile, inexpensive, environmentally-friendly alternative to other microstructuring methods. A wide variety of materials can be synthesized for use in numerous applications ranging from energy storage to biological imaging.

References

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