Microspheres and Nanoparticles from Ultrasound

Final Defense Seminar Won Hyuk Suh November 29, 2006

Improved preparations of various examples of monodispersed[1-4], porous[5-8], hollow, and core-shell[9-16] metal and semiconductor nanoparticles or nanowires[17-18] have been developed. Now titania microspheres and nanoparticles and silica microspheres can be synthesized using an inexpensive high frequency (1.7 MHz) ultrasonic generator (household humidifier; ultrasonic spray pyrolysis; USP, Figure 1).[19-21]

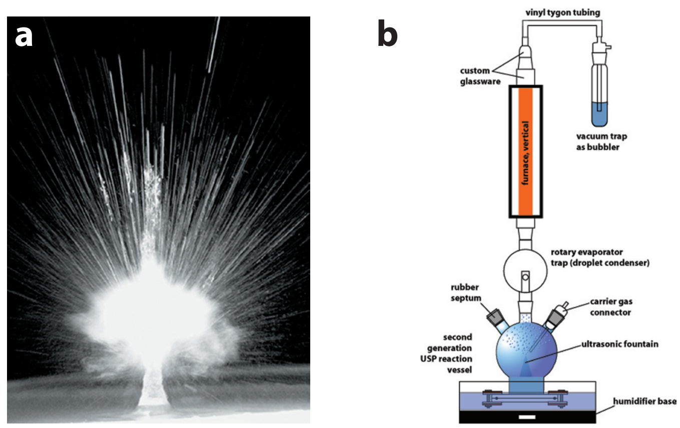

Figure 1. Ultrasonic spray pyrolysis (USP). (a) Ultrasonic fountain from 1.7 MHz frequency. Adapted from reference 19. (b) Vertical USP setup. Adapted from author's Ph.D. thesis.

Morphology and pore size of titania microspheres were controlled by the silica to Ti(IV) ratio and silica particle size. Fine tuning the precursor ratio affords sub-50 nm titania nanoparticles as well. In terms of silica microspheres, morphology was controlled by the silica to organic monomer ratio. In liquids irradiated with high intensity ultrasound (20 kHz; HIUS), acoustic cavitation produces high energy chemistry through intense local heating inside the gas phase of collapsing bubbles in the liquid.[22,23] HIUS[22-25] and USP[26-30]confine the chemical reactions to isolated sub-micron reaction zones, but sonochemistry does so in a heated gas phase within a liquid, while USP uses a hot liquid droplet carried by a gas flow. Thus, USP can be viewed as a method of phase-separated synthesis using submicron-sized droplets as isolated chemical reactors for nanomaterial synthesis (Figure 2).

While USP has been used to create both titania and silica spheres separately,[28,31-33] there are no prior reports of titania-silica composites. Such nanocomposites of metal oxides have been produced, and by further manipulation, various porous structures with fascinating morphologies were generated. Briefly, a precursor solution was nebulized using a commercially available household ultrasonic humidifier (1.7 MHz ultrasound generator), and the resulting mist was carried in a gas stream of air through a quartz glass tube in a hot furnace. After exiting the hot zone, these microspheres are porous or hollow and in certain cases magnetically responsive.

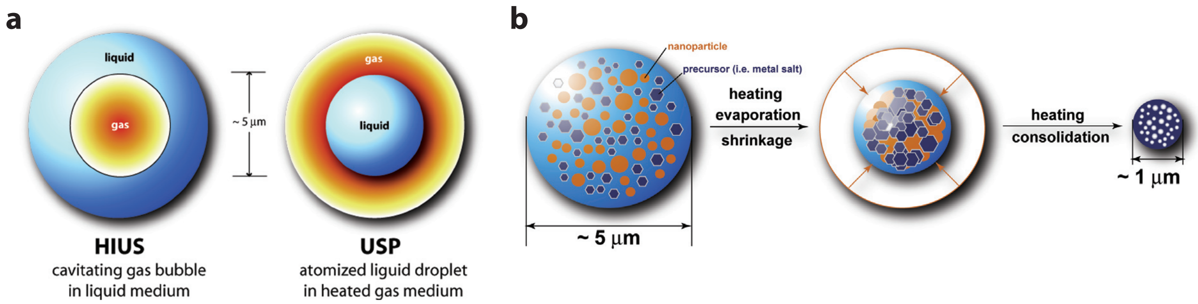

Figure 2. HIUS vs. USP. (a) (left) Cavitating gas bubble inside liquid medium using 20 kHz ultrasound. (right) Nebulized liquid droplet in heated gas medium using 1.7 MHz ultrasound. (b) USP synthesis of a nanocomposite microsphere from a droplet. All schemes adapted from author's Ph.D. thesis.

In the case of titania microspheres, they are rapidly taken up into the cytoplasm of mammalian cells and nearly noncytoxic. Small molecules like Rhodamine and DHED (dehydroevodiamine HCl; Alzheimer's disease therapeutic) can be delivered along with them. Furthermore, synthesis of carbon nanoparticles and titanate nanotube species are possible utilizing these microspheres. Characterizations were done by SEM, (S)TEM, optical/confocal microscopy, XRD, XPS, EDS, SAED, zeta potential, and BET (Figure 3).

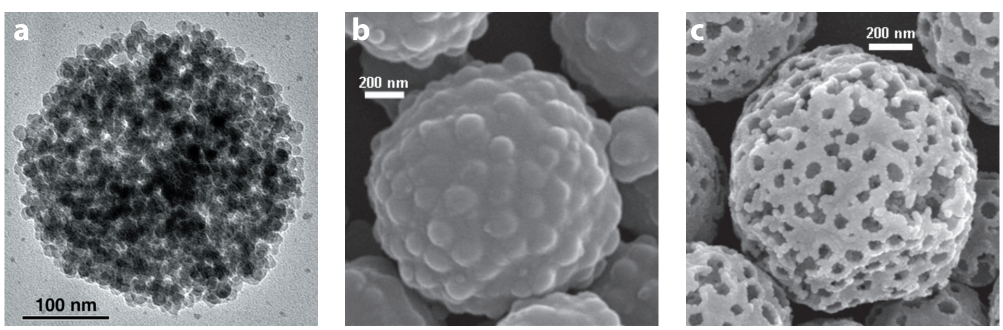

Figure 3. USP microspheres. (a) Porous, magnetic silica microsphere. (b) 70-100 nm silica encapsulated anatase phase titania microsphere. (c) Porous titania microspheres from b. All images adapted from references 19, 20, and author's Ph.D. thesis.

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