

Porous Materials Prepared by Ultrasonic Spray Pyrolysis

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Ultrasonic spray pyrolysis (USP) is a simple aerosol synthetic technique.¹ A schematic of a laboratory-scale USP setup is shown in Figure 1A, and a photograph of the atomization chamber is shown in Figure 1B. The base of a household humidifier, equipped with an ultrasonic transducer, provides the energy necessary for liquid atomization. A fine mist of precursor droplets (diameters $< 5 \mu\text{m}$) is carried by a gas into a furnace where solvent evaporation and precursor decomposition occurs. Product particles are then collected in bubblers positioned at the end of the furnace; byproducts are either dissolved in the collection media or flushed out of the system by carrier gas. Using this technique, both fine powders² and nanoparticles³⁻⁵ have been produced. Precursor droplets also can be deposited onto heated substrates, allowing for the production of films.^{6, 7} There are numerous examples of metal oxide and metal chalcogenide production using USP,^{1, 2} and shown in Figure 1C is a representative scanning electron micrograph (SEM) of MoS_2 particles prepared by traditional USP.

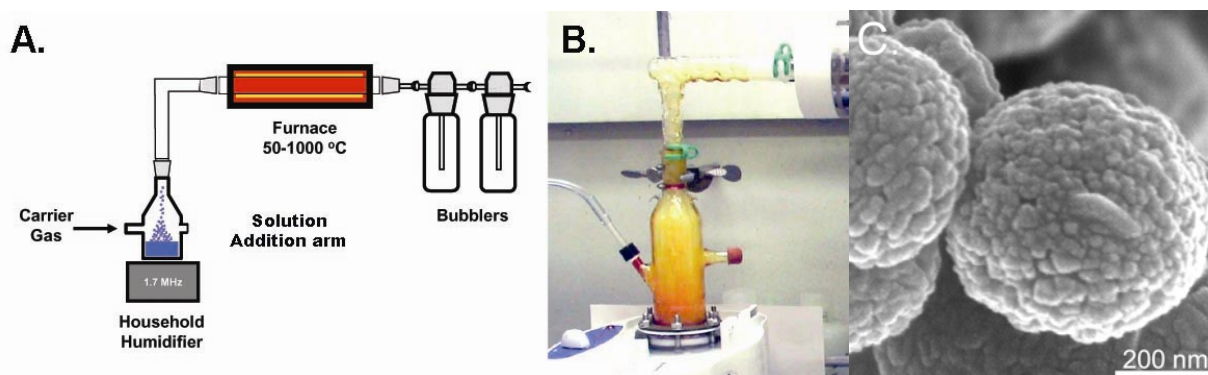


Figure 1 (A) A schematic of a laboratory-scale USP setup. (B) A photograph of the atomization chamber. (C) A SEM image of MoS_2 particles prepared by USP.

USP produced powders are typically comprised of submicron, dense particles; however, depending on a material's applications, porous particles are more desirable. Here, porous particles are prepared using two newly developed templated aerosol methods. In the first approach, a sacrificial template is added to the precursor solution, allowing for composite formation via USP.^{8, 9} Post-collection chemical treatment removes the template and introduces pores into the product particles.^{10, 11} In the second approach, a *temporary* salt template is generated *in situ* which then is removed via aqueous workup.

The first approach was used to prepare porous MoS_2 .¹² MoS_2 is an important industrial catalyst used for the hydrodesulfurization (HDS) of petroleum feedstocks; however, its overall performance is limited by its layered structure which inhibits dispersion of the catalytically active site. The preparation of porous MoS_2 could increase its utility for HDS. Here, colloidal SiO_2 was added to a solution of ammonium tetrathiomolybdate, $(\text{NH}_4)_2\text{MoS}_4$. USP at $700 \text{ }^\circ\text{C}$

produces a SiO₂/MoS₂ composite, and post-collection HF treatment selectively removes the SiO₂, producing high surface area, porous MoS₂ (up to 250 m²/g achievable). TEM images of the SiO₂/MoS₂ composite, as prepared and after HF treatment, are shown in Figures 2A and B. Significantly, these porous MoS₂ powders display enhanced thiophene HDS activity (Figure 2C).

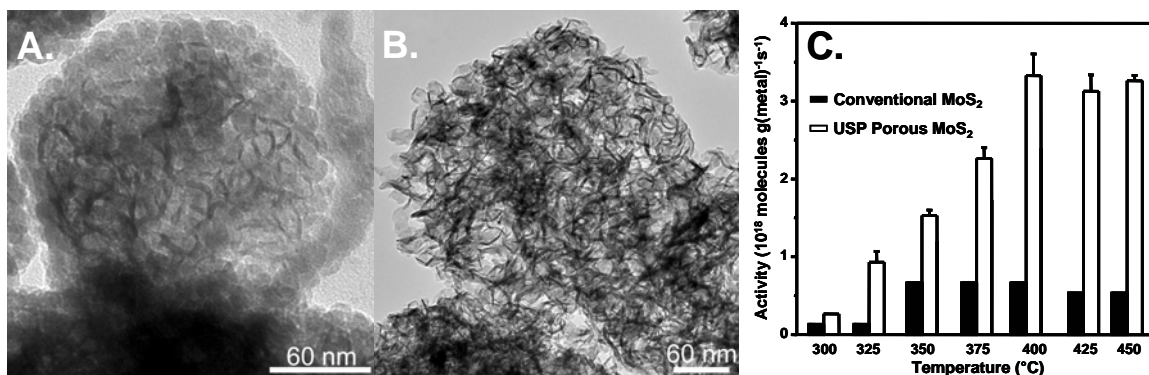


Figure 2 (A) TEM of SiO₂/MoS₂ composite prepared by USP. (B) TEM of porous MoS₂, prepared by HF treatment of the USP composite. (C) Steady-state thiophene HDS activity measurements for porous MoS₂ prepared by USP as compared to conventional MoS₂.

The second approach was used to prepare meso- and macroporous carbon powders which could be useful as adsorbents, catalyst supports, chromatography materials, and more.¹³ Here, organic salts (e.g., alkali halocarboxylates) were selected so that upon thermal decomposition, only small carbon moieties (i.e., C, CH, CCl) and the corresponding alkali halide are produced. The carbon species react with one another to produce a carbon network while the generated salt acts as a *temporary* pore template. Collection in water bubblers removes the generated salt.

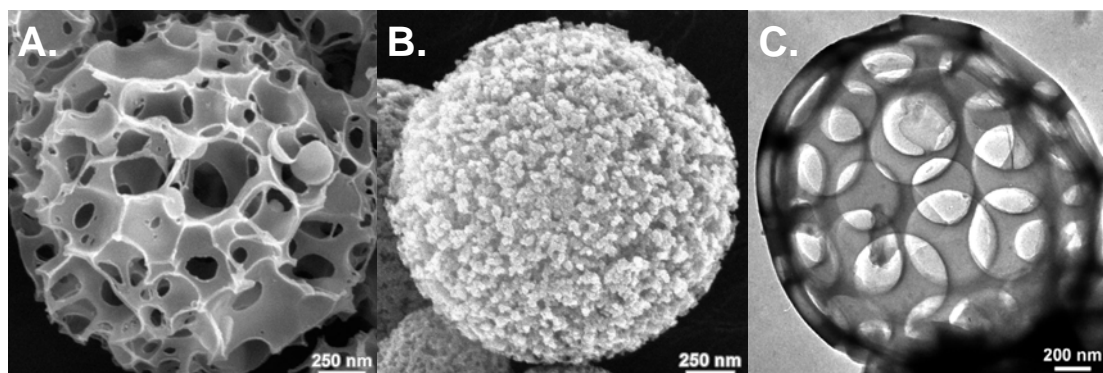


Figure 3 EMs of washed carbon materials prepared by USP. (A) SEM of sodium chloroacetate product. (B) SEM of lithium dichloroacetate product. (C) TEM of lithium glycolate product.

Full characterization of the carbon materials reveals the formation of thermally robust meso- and macroporous networks, in addition to core-shell spheres. Representative EMs are shown in Figure 3. Evaluation of the precursors' decomposition behavior indicates that the relative order of precursor melting, salt elimination, and decarboxylation is responsible for the morphology (and subsequently the surface area) of the resulting material.

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