

Sonochemical Preparation of Hollow Nanospheres and Hollow Nanocrystals

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The development of new nanometer and micrometer morphologies for inorganic materials that may open new opportunities in catalysis, microelectronics, and photonics.^{1–5} One successful approach has deposited inorganic materials on polymeric templates;^{3–5} the use of polymer templates, however, is limited by high-temperature instability. Spherical silica particles have also been exploited as a template for the preparation of hollow mesoporous polymer and carbon materials,^{1–3} but uniform deposition of inorganic material on small silica particles is often problematic due to the lack of coating techniques and poor surface interactions under the usual experimental conditions. We have designed a sonochemical deposition of inorganic materials on nanometer silica spheres that overcomes these problems. This approach makes use of dual effects of ultrasound: (1) the thermal decomposition of organometallic precursors which occurs in the localized hot spots (with temperatures of ~ 5000 K)⁶ to form nanometer-sized inorganic particles^{7–10} and (2) the removal of surface contamination which helps to adhere the inorganic clusters more uniformly.¹⁰ Here we report a simple sonochemical method to prepare hollow MoS₂ and MoO₃ spheres. Further, we find that the hollow MoS₂ is an extremely active catalyst for hydrodesulfurization (HDS) of thiophene. In addition, the thermal annealing of MoO₃ hollow spheres results in the unusual formation of *hollow crystals* with truncated cubic morphology.

Ultrasonic irradiation of a slurry containing Mo(CO)₆ (1 g), S₈ (300 mg), and nanometer silica spheres (1 g) in isodurene under Ar flow yields a MoS₂-coated silica composite.¹¹ The MoO₃/SiO₂ was obtained by a similar manner in the presence of air and absence of S₈. The initial product MoS₂/SiO₂ and MoO₃/SiO₂ materials were washed with pentane and dried under vacuum at 100 °C; yields are essentially quantitative. TEM¹² of MoS₂/SiO₂ and MoO₃/SiO₂ intermediate composites showed uniform coating of Mo species on the SiO₂ surface. Washing the MoS₂- or MoO₃-coated silica with 10% HF in aqueous ethanol yielded hollow shells of the MoS₂ and MoO₃ (presumably by etching through defects in the shell). EDX and elemental analysis confirmed the removal of silica by HF and the absence of any F contamination. Annealing at 450 °C under 10% H₂S/H₂ flow removed any O contamination of the hollow MoS₂ from etching.

The TEM of the hollow MoS₂ nanoparticles shows a uniform shell thickness without collapse of the shell during preparation (Figure 1). The higher-magnification image shows the presence of disordered lattice fringes (interlayer fringes ≈ 6.2 Å) in the initial MoS₂ hollow spheres. The external surface of the hollow MoS₂ is very rough with a high concentration of surface defects. Alternatively, smooth-surfaced hollow MoS₂ can be created by annealing the MoS₂/SiO₂ at ~ 700 °C before HF etching. The evidence for formation of *hollow* spheres is seen in both the electron transmission density (ETD) and energy-dispersive X-ray (EDX) analysis spatially resolved across a sphere using high-resolution STEM. The ETD measurements across a sphere show less electron beam transparency at the edges (due to the shell thickness) than at the center of the

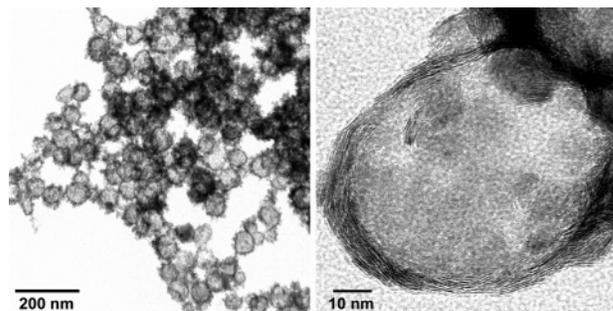


Figure 1. TEM micrographs of sonochemically prepared hollow MoS₂ nanospheres after thermal annealing at 450 °C.

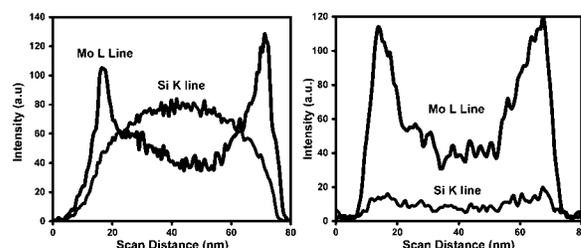


Figure 2. EDX line analysis across the single particles: (a) MoS₂/SiO₂ as initially prepared, (b) hollow MoS₂ after HF acid etching.

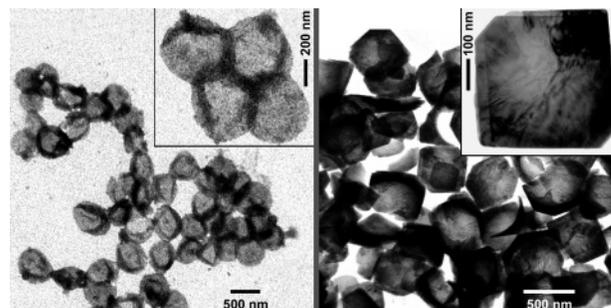


Figure 3. TEM micrographs of sonochemically prepared hollow MoO₃ nanospheres. (Left) After HF etching of MoO₃/SiO₂, but before thermal annealing. (Right) After thermal annealing at 350 °C; insets are at higher magnification, scale bars as shown.

particle (due to the inner void). Figure 2 shows the EDX line analysis across a single MoS₂/SiO₂ sphere and across a hollow MoS₂ particle. In both spectra, the Mo L line decreases from the outer wall in toward the center. The Si K line of the MoS₂/SiO₂ composite sphere shows a gradual increase from the edge to the center, revealing the presence of the inner silica core. After HF etching, the Si K line is essentially gone, showing that the silica core has indeed been removed, leaving a hollow shell.

Similarly, the TEM of hollow MoO₃ (after HF etching) shows the presence of stable and monodispersed hollow particles (Figure 3). Interestingly, the hollow MoO₃ spheres after annealing at 350 °C are converted to truncated cubic *hollow crystals*. The external

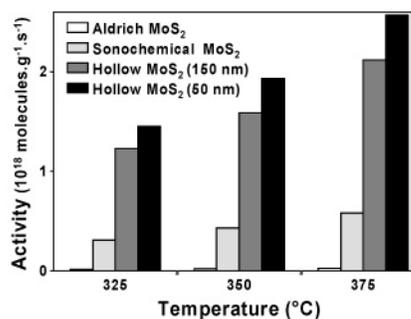


Figure 4. Catalytic activity for hydrodesulfurization of thiophene at 325–375 °C after 24 h over sonochemically prepared hollow MoS₂ nanospheres compared to sonochemically prepared MoS₂ nanoparticles,¹¹ and commercially available micronized powder.

surface of the MoO₃ undergoes a surface reformation to give a stable sharp-edged morphology with a spherical hollow void (Figure 3, right). The ETD and EDX line analysis confirm the hollow core. MoO₃ is normally a layered material, and solid crystalline rods show an orthorhombic growth pattern¹³ reminiscent of the hollow crystals we observe.

For comparison, we also tried an alternative, nonsonochemical preparation of MoO₃/SiO₂, using impregnation of ammonium hexamolybdate onto silica spheres in an aqueous solution followed by thermal treatment at 450 °C and silica removal by HF. In contrast to the sonochemically prepared material, the TEM examination of the conventional MoO₃ residue after HF etching shows an irregular array of holey MoO₃ masses (Supporting Information) due to the nonuniform coating of MoO₃ on the silica surface typical of conventional impregnation.

The optical absorption bands of hollow MoS₂ indicate that its semiconductivity is preserved. The visible spectra show a broad band at 420, 430, and 460 nm, respectively, for nanostructured sonochemically prepared MoS₂ (particle diameter ≈ 3 nm⁹), 50 nm diameter hollow MoS₂, and 150 nm diameter hollow MoS₂ (Supporting Information). This band is due to a direct transition (C excitons) from deep in the valence band to the conduction band; the C exciton for bulk MoS₂ is at ~490 nm.¹⁴ The observed blue shifts of nanostructured MoS₂ are partly attributable to the quantum size effect and increase as particle size or domain decreases. In contrast, the higher wavelength absorption region of hollow MoS₂ shows two broad transitions around 660 and 610 nm, corresponding to the A and B excitonic transitions (at ~655 and ~580 nm for bulk MoS₂).¹⁴ Tenne⁵ found that the wavelength of the exciton bands of inorganic fullerene MoS₂ depend on the number of layers of MoS₂. The broad nature of the absorption bands of sonochemical hollow MoS₂ may be due to imperfections and disorder in this nanocrystalline material. The interplay of strain, quantum confinement, and number of interacting layers is complex, however, and not readily separated.^{5,14}

The HDS of thiophene over sonochemical and commercial catalysts was examined using a single-pass microreactor from 325 to 375 °C.¹⁵ Catalytic activity after 24 h of catalysis are shown in Figure 4 for sonochemical, hollow, and commercial MoS₂ catalyst. The HDS activity hollow MoS₂ is substantially superior to both sonochemically prepared nanostructured and conventional micronized MoS₂ powders (Aldrich, <2 μm diameter). The MoS₂ basal plane is largely inert, while the edges of the MoS₂ layer expose Mo atoms for the HDS reaction (for this reason, HDS activity should *not* be normalized to total surface area).¹⁶ The catalytic activity is therefore highly anisotropic and strongly dependent on the ratio of edge sites to basal plane area. The superior HDS activity of the sonochemical hollow MoS₂ may be due in part to access to

the interior surface of hollow MoS₂ and in part to the high density of edge defects observed in the micrographs. At annealing temperatures above 450 °C, we observe decreased catalytic activity, consistent with an expected reduction in the number of defect sites. It is notable that both inorganic fullerene MoS₂ and MoS₂ nanotubes *fail* to show any significant HDS active, due to the absence of edge sites.⁵

In conclusion, hollow MoS₂ and MoO₃ nanospheres have been prepared by sonochemical deposition on silica powder followed by hydrofluoric acid etching. The superior catalytic HDS activity of sonochemical hollow MoS₂ catalyst is likely to arise from increased surface defects and from access to both the inner and outer surface of the hollow particles. Surprisingly, upon heating, *hollow crystals* of MoO₃ with sharp-edged truncated cubes with inner voids are formed from the initial spheres. We believe this procedure will be easily generalized for the preparation of other hollow inorganic nanostructured materials.

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Supporting Information Available: Optical spectra and SEM of conventionally templated MoO₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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