Highly Selective Monolayer Sorbents for Advanced Analytical Applications

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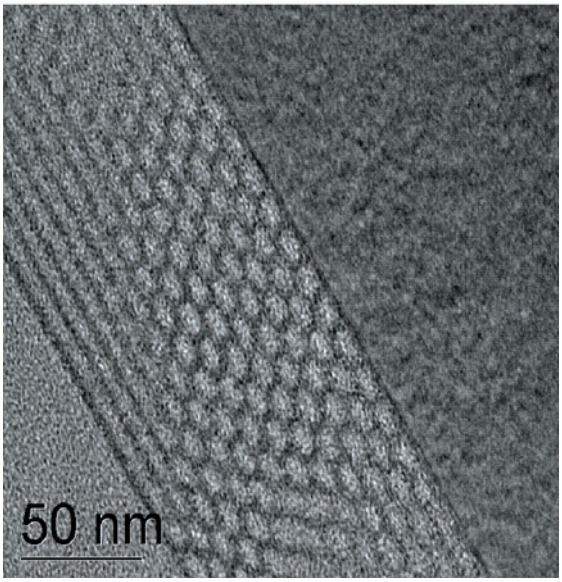
◆ This research focuses on the synthesis and understanding of novel nanostructures and monolayers. The work will provide highly effective materials for preconcentration, separation, sensing, and spectroscopy, enabling the development of a wide range of novel measurement technologies for the detection of trace levels of chemical and nuclear materials. ◆

Detecting the presence of hazardous materials is a crucial primary task for first responders, inspection personnel, and those engaged in environmental characterization. Existing assay methods typically are inadequate because they lack the speed, selectivity, or sensitivity needed to provide key information. In many circumstances, the deficiencies could be addressed with high-performance sorbent materials that selectively concentrate the target analyte. In addition to concentrating the target analyte(s), the sorbent should exclude interferents and provide a uniform, well-defined sample matrix for analysis. Sorbents coupled with existing instrumentation could be used for either real-time analysis of the signature species or as a rapid screening method to flag those samples that require more detailed analysis. Sorbents coupled with rugged, compact instrumentation could provide portable, yet highly sensitive, field analyzers that could be quickly reconfigured for new analytes simply by changing the sorbent material. Sorbents used with the detectors may be reusable, renewable, or disposable, depending upon the instrument configuration desired and material chemistries involved. These same sorbents could be used to improve the performance of traditional laboratory techniques. The thrust of this effort is to develop the basic synthetic methods and fundamental understanding to create novel and useful nanostructured sorbent and sensor materials and to understand how the nanoscale structure affects the process of sorption.

Our synthetic effort to date has yielded mesoporous thin films suitable for diverse analytical applications. The resulting mesoporous thin films supported on a substrate are easier to handle and directly assay than particulate (powder) mesoporous material while retaining all the advantages (e.g., high surface area, rapid mass transport). Methods were developed for creation of the thin films on large-area planar surfaces and irregular thermally sensitive surfaces. The films were water stable (to 60°C), and a novel asymmetric cubic "brick wall" phase was observed. This novel phase, illustrated in the photograph, is believed to be due to surface tension effects upon micelles during curing; the forces driving this assembly are currently under investigation. Films were created from 100 nm to 4 μm thick, with 60- to 100-Å-diameter pores and 650 to 800 m^2/g of surface area. We have also synthesized chemically selective monolayers on the mesoporous thin films and found that they have similar or better performance than traditional particulate mesoporous material. Structure-property correlations are being determined.

We demonstrated 10^6 preconcentration of heavy metals from groundwater, river water, and seawater with a thiol monolayer on a mesoporous sorbent. The preconcentration of the metals in the material was sufficient to enable direct measurement of ultratrace concentrations (1 ppb Hg, Cd, Ag, Cr(IV)) in river water with a portable x-ray fluorescence. We aim to understand the nanoscale mechanisms at work in these structures and are using this knowledge to design and build sorbent films targeted at detecting trace signatures.



Transmission electron microscopy images of "brick wall" cubic phase structure in mesoporous silica thin films. The asymmetric cubic phase is believed to be due to surface tension effects upon the templating micelles.