# PREPARATION OF FUNCTIONAL MESOPOROUS FILMS BY THE 3-D REPLICATION OF FILLED BLOCK COPOLYMER TEMPLATES IN SUPERCRITICAL FLUIDS

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Well ordered mesoporous silica and carbon thin films are extremely attractive for many device applications including, catalyst supports, fuel cells, sensors, device layers in microelectronics and separations media. The incorporation of functional materials within a mesoporous film through encapsulation of nanoscale materials significantly increases the utility of these materials for these purposes.

Recently our group has reported a new approach for fabricating mesoporous materials including silicate, carbon and titanium dioxide films that involves the infusion and selective condensation polymerization of metal oxide or carbon precursors within one phase domain of highly ordered, preformed block copolymer templates using supercritical carbon dioxide as the reaction medium.[1-4] The template is then removed to produce the mesoporous film. In this approach template organization silica network formation occur in discreet steps. Consequently the template can easily be doped with active components in specific sub-domains prior to infusion and removal of the template by calcination.

In this talk several examples of materials encapsulation will be discussed. In one example, encapsulation of equine ferritin within mesoporous silica provides a potential route for high performance sensor materials and for devices that rely on isolated anti-ferromagnetic metal oxide clusters. Ferritin is a spherical protein complex found in the spleen and liver consisting of a ~12 nm diameter protein shell surrounding a ~ 8 nm iron oxide-like core. To encapsulate iron oxide clusters in silica, a poly(ethylene oxide)-poly(propylene oxide)-poly(ethylene oxide) triblock copolymer was doped with ferritin prior to infusion of silica into the polymer template. Subsequent calcination removed the template and protein shell to yield the iron oxide doped mesoporous film. In a second example, the mechanical properties of mesoporous metal oxide films were substantially enhanced through the encapsulation of pre-formed silica nanocages by doping the block copolymer template with polyhedral oligomeric silsesquioxanes (POSS) prior to silica infusion. Additional examples of metal nanoparticle encapsulation in silica and carbon using this approach will also be discussed.

1. Tirumala, T. R.; Pai, R.A. Agarwal, S.; Bhatnagar, G. Romang A., Chandler C. Gorman, B. P. Jones, R. L.. Lin E. K. , Watkins, J.J. "Nanoporous Silica Films with Long-ranged Order Prepared from Block Copolymer/ Homopolymer Blend Templates" *Chemistry of Material* **2007** in press.
2. Nagarajan, S.; Pai" R.A.; Russell' T.P.; Watkins, J.J.*; Li' M.; Bosworth, K.S.; Busch,P.; Smilgies' D. M.; Ober, C.K**.** "An Efficient Route to Mesoporous Silica Films with Perpendicular Nanochannels" A*dvanced Materials*, **2007** in press.
3. Pai, R.A.; Watkins, J.J. "Synthesis of Mesoporous Organosilicate Films in Supercritical Carbon Dioxide" *Advanced Materials*, 18 (2), 241, **2006**.
4. Pai, R. A.; Humayun, R.; Schulberg, M. T.; Sengupta, A.; Watkins, J. J. "Preparation of Mesoporous Materials by 3-D Replication of Block Copolymer Templates in Supercritical Fluids" *Science*, **2004**, 303, 507.