Template Based Strategies for the Fabrication of Porous Silicate Films

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The sol-gel process has been routinely used to prepare silicate materials for a variety of different applications including chemical sensors, photonic materials, and solid state electrochemical devices [1-2]. In a typical procedure, tetramethoxysilane (TMOS) is mixed with water in a mutual solvent such as methanol followed by addition of a catalyst such as hydrochloric acid. During sol-gel formation, the viscosity of the solution gradually increases as the sol becomes interconnected to form a rigid, porous structure - the gel [1-2]. Prior to gelation, an aliquot of the silica sol can be spin cast or dip coated on a suitable substrate to form a thin film or poured in a suitable container to form a block monolith. Thin films are commonly used in the development of chemical sensors due to their short pathlength for diffusion, which decreases response times and recovery rates. The properties (*i.e*, pore size, pore connectivity) of silica films are vastly different than silica gel monoliths due to the fact that gelation occurs simultaneously with drying. Films prepared from acid catalyzed silica sols, in particular, are quite dense, leading to a reduction in the mobility and activity of entrapped reagents and the rate at which external molecules can diffuse into the films.

The ability to engineer porosity into these dense materials while simultaneously maintaining most of the promising features will clearly improve their performance in many applications. Among various strategies for the preparation of porous materials, template based sol-gel processing has rapidly gained popularity [3]. In this approach a polymeric network is assembled around a suitable "template" molecule or structure. Upon removal of the template, diffusional pathways and/or microcavities with a specific size, shape, and/or chemical functionality remain in the crosslinked host.

In this work, polystyrene microspheres have been used as the templating entities to fabricate macroporous silicate films with controllable pore size. This procedure involves (1) preparation of the silica sol, (2) doping of the sol with sulfate stabilized polystyrene microspheres of diameter 300 – 1000 nm, (3) casting of the silica sol on a suitable substrate to form a thin film, and (4) removal of the spheres by soaking the film in either toluene or chloroform. The size, number density, and distribution of pores produced in a dense silicate host after template removal have been thoroughly examined via a combination of electrochemical, microscopic, and spectroscopic techniques.

Atomic force microscopy (AFM) reveals that the cavities are formed in the film after template removal. The shape of the cavities mimic the shape of the bottom half of the polystyrene particle. The inner diameter of the cavity is approximately the same size as the diameter of the latex sphere used to prepare the film. The accessibility of the pores to various reagents has also been evaluated using electrochemical methodologies, specifically cyclic voltammetry. In this study, the macroporous film previously cast on an electrode surface has been placed in a solution of an electroactive reagent such as ruthenium hexaammine, potassium ferricyanide, or ferrocene methanol. Faradaic current can be observed due to the diffusion of the reagent through the pores followed by electron transfer at the electrode surface. The magnitude of the current is highly dependent on the charge of the redox reagent. For negatively charged reagents, very little current is observed.

In this presentation, these results as well as other approaches to molecular templating will be presented and discussed.

References

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