Fabrication and Characterization of Ordered Nickel Oxide and Cobalt Oxide Monoliths

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High surface area, monolithic materials with hierarchical porosity are of great interest in fields such as separations and catalysis. One such material incorporates SBA-15, which is synthesized using the triblock copolymer Plurionic P123 to template an ordered pore structure at the nanometer scale [1]. There has been extensive research done on the replication of SBA-15 silica particles to form nanowires, but until now, no replication of an SBA-15 monolith has been reported. We report the successful replication of these monoliths in nickel and cobalt oxide.

Metal oxide monoliths were synthesized through nanocasting, which is the process of filling a porous template with material and then removing the template [2]. The silica template used for this procedure was synthesized using a method previously reported [3]. The sol-gel synthesis started with a solution of P123 in 0.02 M acetic acid, followed by addition of tetramethylorthosilicate (TMOS) as a silica source. The solution was then poured into molds and heated for 24 hours at 40 °C and 24 hours at 60 °C. The resulting monoliths then undergo a steam treatment and water treatment for strengthening, followed by calcination to remove surfactant. The resulting silica monoliths have a macropore network that is continuous throughout the monolith, and a highly ordered pore structure within the walls of the macropores.

Replication of the silica monoliths was then performed by nanocasting. This was done with either a saturated cobalt nitrate or nickel nitrate solution. The silica monolith and solution were degassed separately, and then introduced to each other under vacuum to insure pore filling. The impregnated monoliths were then dried for ten hours at 150 °C for ten hours, and then heated to 250 °C for four hours. The process of infiltration and decomposition was repeated three times, and a composite of silica and metal oxide was formed. The silica was then etched away using a 3 M potassium hydroxide solution.

A FEI Tecnai F-20 Transmission Electron Microscope (TEM) and a JEOL-7000 Scanning Electron Microscope (SEM) were used to acquire images. Figure 1a shows the macropore network that runs throughout the silica monolith. These pores have an average size of about 6-7 micrometers. Figure 1b shows the highly ordered mesopores forming the macropore walls. These have an average size of about 6 nanometers. The macroporous (Figure 2a) and mesoporous (Figure 2b) cobalt oxide structure that remains after silica removal shows a very successful replication of both sets of pores. The nickel oxide macropore (Figure 3a) structure looks slightly different than the parent silica, but the mesopores (Figure 3b) still show excellent ordering. We are performing TEM tomography on these materials to visualize the replication of the micropores present in the walls of the mesoporous silica. The replication of these micropores is believed to be critical for producing free-standing replicas of SBA-15 particles. We hope to determine what role the micropores and their replication plays in producing mechanically stable monolith replicas.[4].

References


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Figure 1: a) SEM of silica macropores and b) TEM of silica mesopores (20 nm scale bar)

Figure 2: a) SEM of Co3O4 macropores and b) TEM of silica mesopores (20 nm scale bar)

Figure 3: a) SEM of NiO macropores and b) TEM of silica mesopores (50 nm scale bar)