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SnO_x Nanocrystallites Supported by Silica Nanostructures

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ABSTRACT

We demonstrate the results of a single-step in-situ synthesis that produces surface decoration of partially agglomerated amorphous silica nanospheres (diameter ∼45 nm) with SnO_x nanocrystals of diameter 3–6 nm. The technique would appear to be useful for the dispersal of extremely small tin oxide nanostructures on a silica nanosurface to produce improved sensors and catalysts. Preliminary results indicating improved kinetic activity on this nanoscale are reported.

It has been suggested that nanometer sized particles, properly prepared and treated, might be used to form the high surface area analogues of known catalysts or sensors to provide improved efficiency of existing catalytic[1] or sensor[2] function. This might further be improved through changes in molecular electronic structure and as a result the development of confined regions that accompany the transition to the mesoscopic regime for both the active elements and their substrate supports.[3] To this end, we have recently synthesized dispersed silica (SiO_2) nanospheres[4] in a single-step high-temperature synthesis. As a function of slightly modified experimental conditions,[5] these nanospheres have a nearly monodisperse particle size distribution which, for a given experimental run, can center on a size from ∼45 to 8 nm in diameter. These potential substrate elements can be synthesized over a time frame of approximately 12 h to produce gram quantities of material. Transmission electron microscopy (TEM),[4] X-ray diffraction,[4] and ESR[6] measurements demonstrate that the nanospheres are amorphous and absent of dangling bonds. They have been used to sequester active copper sites for the selective catalytic conversion of ethanol to acetaldehyde[7] in a process that is at least three times more efficient than that using fumed silica produced from the flame hydrolysis of silicon tetrachloride.[8] Further, it has been possible to reduce a Ni(III) solution in an electroless process on the surface of the nanospheres producing a ferromagnetic crystalline nickel coating[6] of variable thickness.

These results are significant as they demonstrate that, by choosing a select high temperature synthesis, it can be possible to produce nanosupports and subsequently nanocatalysts employing far fewer synthesis steps than conventional processes. The nanospheres are produced in a single-step high-temperature synthesis and can be readily treated in a minimum of subsequent steps. Further, the introduction of these synthesis steps allows the formation of a final product with the minimal use of solvents.

While it is desirable to metallize the silica nanospheres to enhance their surface sensitivity through formation of metal or metal oxide coatings, the formation of catalytic copper sites or the metallic coating of the nanospheres (e.g., nickel, silver), as they result from ex-situ processes, does not lend itself readily to the creation of more refractory metal oxide heterostructures. Within this framework, we include the dispersal of SnO, SnO_2,[2] or TiO_2[9] nanostructures on a silica surface to produce improved sensors or photocatalysts. Here, we report the results of a single-step in-situ synthesis that demonstrates the surface decoration of silica nanospheres with crystalline SnO_x nanocrystals (Figure 1). SnO_x, the most successful chemical sensor,[2,10,11] has been used for the detection of reducing gases. It has been used in environmental sensor "nose" arrays and responds to several gases including CO. The tin oxide usually consists of compressed powders with a grain size typically on the nanometer scale and commonly doped with catalytic metals to enhance chemical selectivity. The particle size strongly influences the sensor response, resulting in higher sensitivity with smaller particle size and long-term stability and reduced baseline drift at smaller particle dimensions (∼10 nm).[10,11] Thus, the ability to disperse extremely small SnO_x ($x = 1-2$) nanocrystallites on a nanostructured silica substrate can have important consequences for future sensor technology. In addition, it can play an important role in advanced acid catalysis[12,13] and in the detection of algacides.

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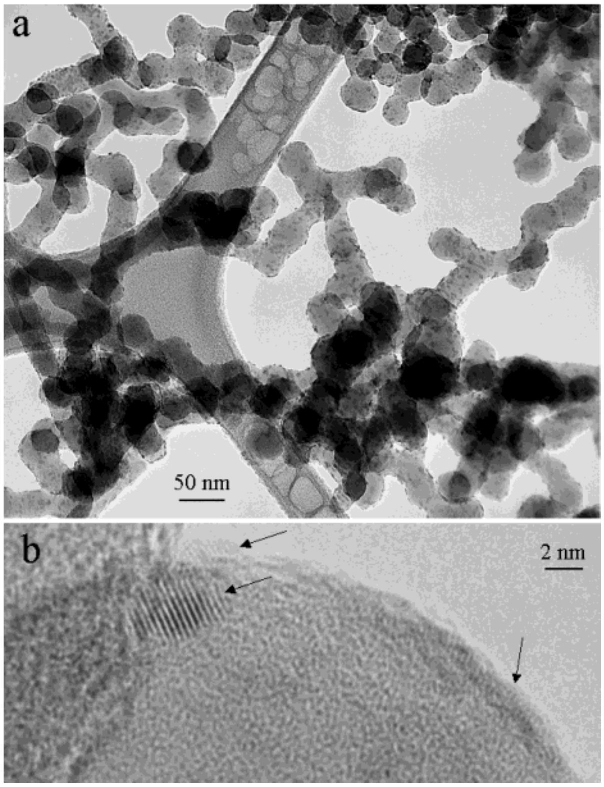

Figure 1. (a) TEM image of an as-synthesized sample showing agglomerating silica nanostructures of diameter ∼45 nm covered by SnO_x nanoclusters. (b) High-resolution TEM image showing the crystalline structure of the SnO_x nanoclusters.

Silica nanospheres have been synthesized from a 50/50 Si/SiO_2 mixture at a temperature close to 1400 °C.[4] The distribution of nanospheres and their size is controlled by adjusting system gas flow rates, total gas pressure, and temperature. The apparatus used in the synthesis of the SnO_x/SiO_2 heterostructure depicted in Figure 1 was operated with a few significant modifications from those discussed previously.[4,12,13] UHP argon entrainment gas was again made to pass over a crucible located in the central region of the inner tube of a sealed double concentric alumina tube-oven configuration heated by a Lindbergh-Blue furnace. The parameters controlled in this experiment were (1) argon flow rate, (2) total tube gas pressure, (3) central region temperature, and (4) temperature gradients to the end regions. The alumina crucible (Coors Ceramics) used to contain the reactant mixture used in these experiments was heated to 1300 °C and maintained for 12 h. It contained a silicon−silica (Si/SiO_2 ∼ 1:1) mixture into which was interspersed a small percentage of SnO (∼2%) and a manganese catalyst (∼1%). The argon flow rate was 100 sccm, while the total tube pressure for the sealed inner tube[4] was ∼300 Torr, controlled by a Welch 1402 mechanical pump. We observed the deposition of nanosphere agglomerates (impregnated by nanocrystalline SnO_x islands) deposited on both the wall of the inner alumina tube in the 900−1000 °C temperature interface region[4] and on a cold plate positioned at the downstream onset of the interface region.[4]

The transmission electron micrographs depicted in Figure 1 were obtained at 200 kV using a Hitachi HT-2000 TEM.

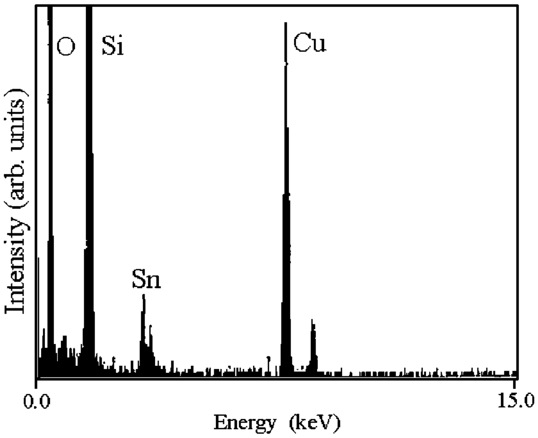

Figure 2. Energy-dispersive X-ray spectrum illustrating the presence of Sn, O, and Si in the sample as synthesized decorated silica nanospheres. The copper peaks come from the grid used to support the specimen.

The chemical composition of the SnO_x impregnated SiO_2 nanosphere agglomerates was determined (Figure 2) by energy-dispersive X-ray spectroscopy (EDS).

Figure 1 corresponds to transmission electron micrographs (TEM) of partially agglomerated monodisperse SiO_2 nanospheres of diameter ∼45 nm, on which are interspersed small SnO_x islands. The assessment of the silica nanospheres and the attribution of the small dispersed islands of tin oxide (SnO_x) are aided by the EDS spectrum, displayed in Figure 2, which clearly indicates the presence of silicon and oxygen associated with the larger nanospheres and tin and oxygen (at considerably lower concentration) associated with the SnO_x islands. The SnO_x nanoclusters are distributed approximately uniformly over the surface of the silica nanostructures. Their sizes are between 3 and 6 nm. A quantitative EDS microanalysis shows that the Si/Sn ratio is approximately 25:1 across the silica nanosphere supports. No evidence is found for SnO_x dispersed within the silica. The high-resolution transmission electron microscopy (HRTEM) images of the SnO_x nanoclusters given in Figure 1b and the Moire patterns clearly demonstrate that they are crystalline. These nanocrystallites would appear to be among the smallest distinct SnO_x structures generated to date. The SnO_x nanoclusters cover the surface of the silica nanospheres as indicated by the arrows at the right-hand side of Figure 1b. The precise crystal structure of the SnO_x crystallites is difficult to assess in the present experiments. However, it is not inconsistent with the rutile structure of SnO_2.

We have carried out studies to address the catalytic activity of these SnO_x coated silica nanopheres.[14] The hydroxylation of phenol has been used as a probe for the oxidation activity of titanium silicate (TS-1)[15] supported Fenton's catalysts[16] as well as other catalysts including zeolites.[17] This probe reaction, which gives a good measure of the intrinsic activity of the tin oxides, using the rate of disappearance of phenol, has now been evaluated. Preliminary tests on a series of SnO_x-based catalysts including reagent grade SnO_2,SnO, and naked silica suggest a considerable increase in activity for the phenol conversion by the silica-supported SnO_x nanocrystallites.

The details of our catalytic studies will be presented elsewhere.[16] Briefly, each catalyst was dried at 100 °C for at least 30 min before the phenol oxidation reactions were attempted. For each catalyst, a standard solution of 1.79 mL of 11.7 mM phenol solution (0.021 mmol) was combined with 9.6 mL, 3 wt %, H_2O_2 (8.5 mmol). These initial mixtures were analyzed in a Buck Scientific BLC-20 isocratic liquid chromatograph (HPLC) equipped with a C_{18} column. After noting both color and texture, 0.74 mmol of each catalyst was added to each solution. The reactions were monitored on the HPLC for at lease a three-day period, and data was recorded on the HPLC for each sample at least twice per day. For the SnO_x on silica nanospheres, we have determined first-order rate constants differing by at least a factor of between five and twelve times those for reagent-grade SnO and SnO_2, respectively,[14] as all three materials are found to be reactive. This comparison is for total material mass, which suggests that the silica-supported tin oxide is much more active. No catalytic activity was noted for undecorated silica, and a blank run, using the reactants catalogued above but no catalysts, showed very little conversion for runs up to 70 h.

We suggest that by identifying a select set of conditions for the high-temperature in-situ synthesis, we have demonstrated that it is possible to cover the surface of a substrate composed of partially agglomerated silica nanospheres with small interspersed islands of nanocrystalline SnO_x in a single-step process. These materials demonstrate significant kinetic activity.[14] Based on previous trends, the formation of these crystalline nanostructures on the silica substrate may also have implications for the improvement of SnO_x chemical sensors.[18] Recent efforts, which have led to the first synthesis of tin oxide nanostructures including wires, disks, ribbons, and nanotubes,[19] suggest that it will be possible to enhance the density of the tin oxide islands depicted in Figure 1; however, this will require a distinctly different synthesis. If this approach can be extended to other metal oxides such as TiO_2, it may be possible to considerably improve metal oxide photocatalysts.[20,21] Further, we note that this synthesis mode is, within itself, environmentally benign.

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