

## **Use of alkoxide sol-gel process for linear assembly of oxide particles**

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The alkoxide sol-gel process is widely used to form powders, coatings, thin films and fibers of oxides and glasses. The processes of hydrolysis and condensation in the sols prepared from tetraethylorthosilicate (TEOS) have been well studied. When an acid is used as a catalyst, linear chains having a  $-\text{Si-O-Si}-$  backbone with OH or alkoxy side groups on Si are formed, while with a basic catalyst, a 3 dimensional network structure is formed. The presence, during the sol-gel process, of polymeric units whose structure can be easily controlled by changing the parameters such as pH of the sol, offer the possibility of generating the corresponding assemblies of particles. In the present work, we demonstrate the use of such polymeric structures in a silica sol for the assembly of oxide particles.

A TEOS sol was prepared using 1 ml TEOS, 95 ml ethyl alcohol and 1 ml water. The pH of the solution was adjusted to desired value ( in the range 3 to 5) using diluted HCL. The solution was stirred for 1 h . The resulting sol was allowed to age for different aging times to allow some polymerization to proceed. A suspension of  $\text{ZrO}_2$  particles (200 nm nominal size, TOSOH, Japan) in ethanol was prepared. The suspension was added to the sol and the reactions were allowed to proceed further for different reaction times in the presence of the particles. A drop of this sol was then deposited on a clean glass substrate and allowed to dry. It was then examined in a scanning electron microscope.

Various arrangements of particles in the dried gel were observed. These included isolated particles, small clusters, large flocs and, interestingly, large chains with small side branches. The types of structures that form appear to depend on several parameters of which the most important are the pH of the sol, concentration of the particles and the rate of drying. Under suitable conditions, long chain like features consisting of the oxide particles, are observed. These chains were often more than 10  $\mu\text{m}$  long with smaller side branches. Considering the nature of the arrangement of particles, particularly the long chain structures observed by us, it appears that the polymer chains are acting as templates for the particles. Several samples with variation of parameters such as pH, the aging time and the reaction time were examined. At  $\text{pH} > 4$ , mostly flocculated structures were observed while at  $\text{pH} < 3$ , small clusters of particles were most common. However, the long chain structures were nearly always observed when the pH of the sol was adjusted between 3 and 3.5 .

Our results thus show that it is possible to use polymeric units forming during the alkoxide sol-gel reaction as templates for the assembly of  $\text{ZrO}_2$  nanoparticles. The method should be applicable to other oxides as well as to semiconductor and metal particles.