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Modification of Surface Properties of Nanoparticles by Plasma Polymerization Techniques

William J. van Ooij, Department of Materials Science and Engineering, University of Cincinnati, Cincinnati, OH 45221-0012, USA

Nanoparticles of inorganic materials inherently possess a very high surface energy. For many applications of such particles in nanostructured materials, it would be beneficial to tailor their surface energy as well as their surface reactivity by a suitable surface treatment. In this paper we will explore the suitability of surface modification by plasma polymerization. This surface modification technology has been extensively used by us for the surface modification of larger particles for several years now. Several different types of reactors have been designed and built for this purpose in our laboratory. Plasma polymerization of nanoparticles is very challenging, in view of the dimension of the particles. Vacuum fluidized-bed plasma treatment, for instance, is not possible with nanoparticles, as they cannot be fluidized and filtered. However, we have adopted a relatively simple approach, in which the particles are vigorously stirred at the bottom of a flask while an RF-generated plasma containing an organic monomer is aimed at the bed of the particles. In this approach, we have been able to deposit 2-10 nm plasma-polymerized films uniformly on nanoparticles of 30-50 nm diameter. Particles thus treated show a dramatic change in their properties.

Several applications of this technology will be presented and discussed in this paper. They will include the following.

1. Treatment of Al_2O_3 nanoparticles–It will be shown that a uniform 2 nm coating of plasma-polymerized pyrrole on 30 nm oxide particles can be obtained which dramatically alters the properties of the particles when compacted under high pressure at relatively low temperatures. Coating of particles of these dimensions followed by compacting can become a novel route to the manufacture of nanostructured materials.
2. Treatment of ZnO nanoparticles–A coating of plasma-polymerized acrylic acid (PP-AA) was deposited on nanoclustered ZnO particles. The clusters had a very high surface area. The deposition of the PP-AA film was optimized for minimum water solubility and maximum retention of carboxylic acid groups. Thus, the clusters had become an effective ion exchanger material. Results will be presented of the removal of nickel ions from water by the treated nanoclusters.
3. Treatment of carbon nanotubes–The purpose of a plasma-polymerization surface treatment here was to reduce the strong interaction between the nanotubes which are extremely hard to disperse in organic polymers. A coating of 2 nm on the inner and outer surfaces of the tubes led to a very high dispersibility in solvents like toluene.
4. Treatment of clay nanoparticles–The objectives of this project is to develop novel fillers for rubber and other polymers which could replace carbon black. Starting with inert clays of nanoparticle dimensions, the surface was tailored by depositing a film of plasma-polymerized acetylene on the surface of the particles. The conditions of the plasma were optimized so as to obtain polymer films with sufficient reactivity to rubber cure systems so that the particles covalently bonded to the polymer during the cure.

Several other applications of this technology will be described as well, for instance the possibility to develop treatments of water-soluble nanoparticles for slow-release purposes. The equipment requirements as well as techniques to characterize the treated particles such as HR-TEM, TOFSIMS and FTIR, will be discussed. A design for a process scale-up will be presented.