

## **Multi-Layer Coating of Ultrathin Polymer Films on Nanoparticles of Alumina by a Plasma Treatment**

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### **ABSTRACT**

Multi-layer ultrathin polymer films have been deposited on the surfaces of nanoparticles of alumina using a plasma polymerization treatment. The nanoparticles ranged from 10-150 nm in spherical shapes. High-resolution transmission electron microscopy (HRTEM) experiments showed that an extremely thin film of the pyrrole layer (10-20 Å) was uniformly deposited on the surfaces of the nanoparticles. In particular, the particles of all sizes (10-150 nm) exhibited equally uniform ultrathin films indicating well-dispersed nanoparticles in the fluidized bed during the plasma treatment. After single layer coating, hexamethyldisiloxane (HMDSO) was coated again as a second layer onto the surface of pyrrole. Subsequently, a third layer of pyrrole was coated on the top of HMDSO film completing the multi-layer coating process. Time-of-Flight Secondary ion mass spectroscopy (TOFSIMS) experiments confirmed the deposition of these multi-layer thin films on the nanoparticles. The deposition mechanisms and the effects of plasma treatment parameters are discussed.

### **INTRODUCTION**

Surface coating of nanoparticles is an important area in nanomaterials synthesis. Because of their special composition, these coatings possess a unique combination of properties of the inorganic and organic components, for instance hydrophobic, hydrophilic, anti-fogging, anti-fouling, anti-adhesive and/or teflon-like properties in combination with hardness and scratch and abrasive resistance. The combination of mutually chemically interconnected organic and inorganic networks results in coatings with a very low permeability for gases and liquids. Hybrid materials are very suitable for application as coatings on a highly diverse spectrum of substrates including glasses, ceramics, plastic, wood, and metal. Before curing, the coating materials consist of a clear alcoholic solution that can easily be processed by classical application techniques such as dipping, spraying, or spin coating. However, in these previous coating processes, the coatings are quite thick up to the order of microns.

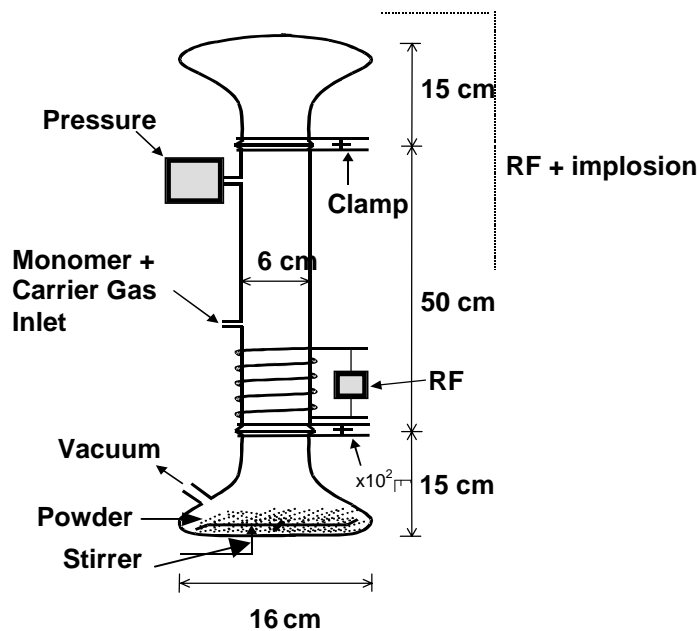
The current trend of developing nanophase materials has motivated an increased need for nanometer-scale structures in a variety of applications. Indeed, it is clear that, in order to achieve unique mechanical, physical, chemical, and biomedical properties, it is necessary to develop novel synthesis routes by which new nanostructures can be developed. In the past, great efforts have been focused on nanoparticle synthesis, assembly, interfaces, dispersions, and functional devices (1-5). Although high volume

(~80 vol.%) polymer coating of nanoparticles has been reported (6), no studies so far have shown uniform deposition of ultrathin films of the order of 10-20 Å on the surface of the nanoparticles, which is, in this letter, referred to as “nanocoating.” The deposited film can also be tailored to multi-layers on a nanoparticle. Nanocoating is of particular importance in electronics, functional devices, new materials synthesis, nanobiomolecular applications, tissue engineering, and drug delivery. Using nanocoating, it is possible to alter the intrinsic properties of materials that cannot be achieved by conventional methods and materials.

For nanoscale ceramics particles, under a well-dispersed condition, it is possible to deposit a thin film of foreign species uniformly on the nanoparticle surfaces and thereby reduce their surface energies. In this study we will address these issues and report experimental data on the deposition of multiple layers of polymer ultrathin films on the surfaces of nanoscale alumina particles by a plasma polymerization process. The deposited thin films are plasma-polymerized pyrrole and hexamethyldisiloxane (HMDSO).

## EXPERIMENTAL DETAILS

In this experiment, a RF-plasma reactor was used for the nanoparticle coating. In this experiment, we have selected nanoscale alumina particles ranging from a few nanometers to 150 nm. This large distribution of particles is particularly useful for the study of deposition experimental conditions for different sizes. The schematic diagram of the plasma reactor for thin film deposition of nanoparticles is shown in Figure 1. The vacuum chamber of plasma reactor consists of a long Pyrex glass column about 80 cm in height and 6 cm in internal diameter (7,8).



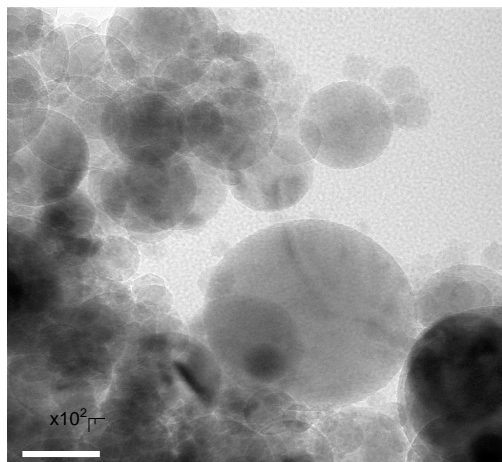
**Figure 1.** Schematic diagram of the plasma reactor for thin polymer film coating of the nano-particles.

The nanoparticles of alumina are vigorously stirred at the bottom of the tube and thus the surfaces of nanoparticles can be continuously renewed and exposed to the plasma for thin film deposition during the plasma polymerization process. A magnetic bar was used to stir the powders. The gases and monomers were introduced from the gas inlet during the plasma cleaning treatment or plasma polymerization. The system pressure was measured by a pressure gauge. A discharge by RF power of 13.56 MHz was used for the plasma film deposition. Before the plasma treatment, the basic pressure was pumped down to less than 200 mTorr and then the plasma gases or monomer vapors were introduced into the reactor chamber. The operating pressure was adjusted by the gas/monomer mass flow rate. The base pressure was less than 200 mTorr. Pyrrole and HMDSO were used as monomers for plasma polymerization. During the plasma polymerization process, the input power was 20 W and the system pressure was 450 mTorr. The plasma treatment time was 240 min. Per batch 40 grams of powder were treated.

For the single layer coating, pyrrole was used as the monomer. Double and triple layers coatings were done after the single layer coating batch. For the double layer coating, pyrrole was coated for 240 min followed by another 240 min of HMDSO coating under the same condition. For the triple layer coating, the same procedure for double layer coating was employed followed by a second pyrrole coating for 240 min.

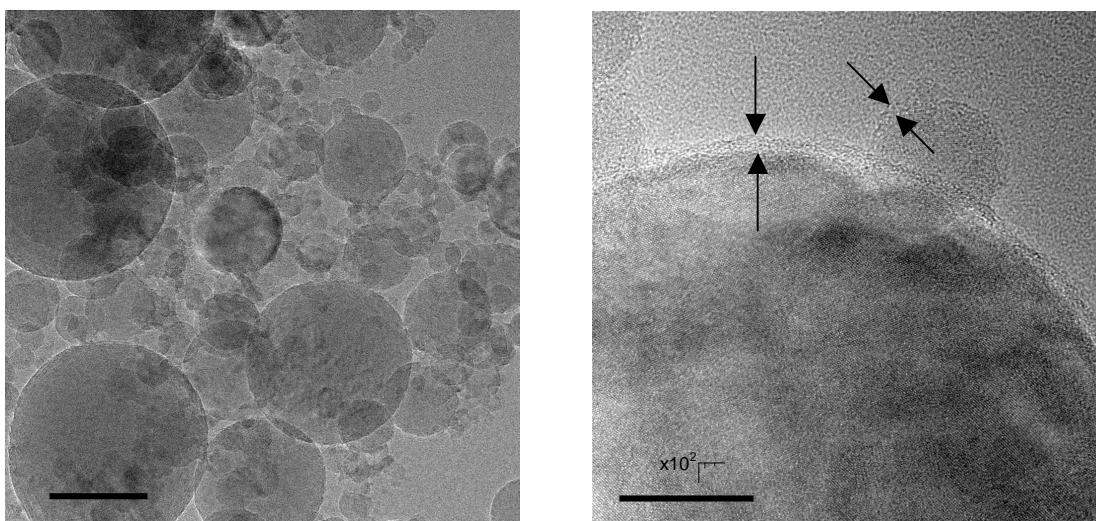
After the plasma treatment, the nanoparticles of alumina were examined by using transmission electron microscopy (TEM), scanning electron microscopy (SEM), x-ray diffraction (XRD), and Time-of-Flight secondary ion mass spectroscopy (TOFSIMS). The high-resolution TEM (HRTEM) experiments were performed on a JEOL JEM 4000EX TEM; the TOFSIMS analyses were performed on an ION-TOF Model IV instrument.

In transmission electron microscopy, the original and coated  $\text{Al}_2\text{O}_3$  nanoparticles were dispersed onto the holey-carbon film supported by Cu-grids for the TEM operated at 400 kV. Figure 2 shows the high-resolution transmission electron microscopy (HRTEM) image of the original, uncoated alumina nanoparticles. As can be seen in this figure, the particle size ranges between 10 nm and 150 nm. The particles are also spherical in shape for all sizes.



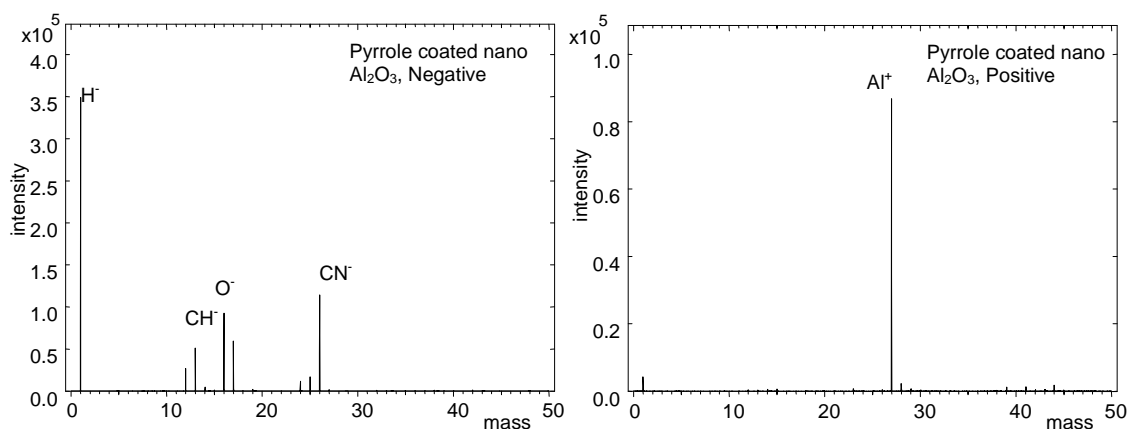
**Figure 2** TEM image showing the uncoated alumina nanoparticles. The scale bar is 50 nm.

Figure 3a is the HRTEM image of the coated particles. Compare to Figure 2, one can see a bright ring on the particle surfaces, which is the result of the polymer coating. Figure 3b is a high magnification image showing a uniform coating on the particle surfaces. In this figure one can see not only that the large particle ( $d \sim 100$  nm) in the photograph is well coated, but also the two smaller ones with a diameter of 15 nm. The coating thickness is approximately 2 nm all the way surrounding the particle surfaces. Particularly interesting, although these particles have different diameters, the coating remains the same thickness indicating the uniform distribution of polymer atoms in the plasma chamber. The coating layer is amorphous based on the HREMs of different particles. In contrast, the images of the original particles (Figure 2) do not show the amorphous layer. Thus, we are certain that the observed layer is due to coating rather than an artifact in TEM observation. For multiple-layer-coated nanoparticles, however, we did not observe any distinguishable layers of pyrrole and HMDSO. The coated layers exhibit amorphous-like structures similar to the TEM images shown in Figure 3. More detailed HRTEM work is currently under way for the double- and triple- layer coatings.



**Figure 3.** TEM images showing coated nano alumina particles. The scale bar is 50 nm in Fig. 3a and 10 nm in Fig. 3b. The arrows in Fig. 3b indicate the polymer coatings.

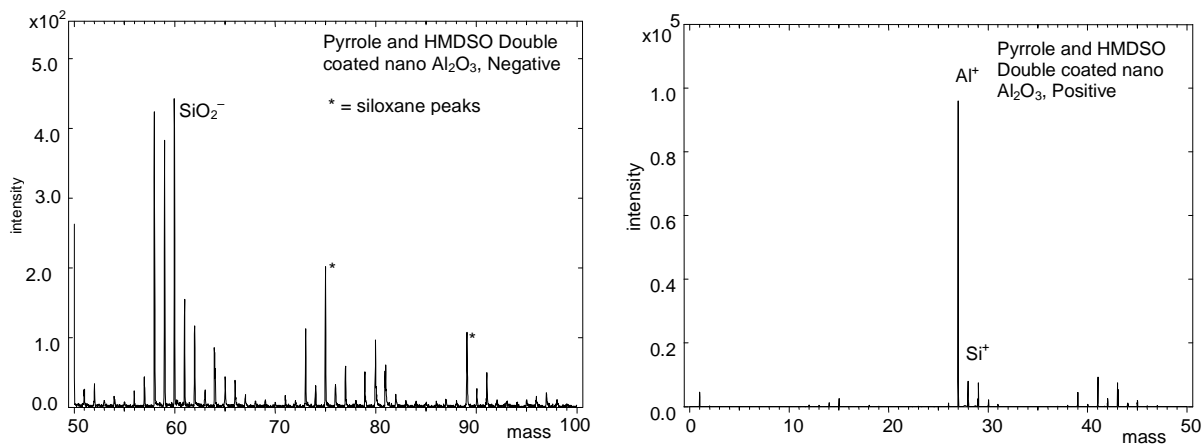
Figure 4 shows the SIMS spectrum of pyrrole-coated nanoparticles of alumina. As can be seen in this figure, the strong pyrrole peaks indicate the surface coating of the nanoparticles and are consistent with the HRTEM data presented in Figure 3. The spectrum of the untreated powder shows an appreciable intensity of magnesium in the surface layers. There are also traces of sulfur, iodine and organic material. The treated aluminum oxide shows the characteristic cluster pattern of plasma-polymerized pyrrole (9). The intense peak at  $-26$  m/z ( $CN^-$ ) is typical of all nitrogen-containing functionalities. The intense peak of  $Al^+$  at  $+27$  m/z is *not* the result of an incomplete coverage of the particles by the plasma polymer, but is caused by the intense sputtering of aluminum atoms from the particle surface during the initial phase of the plasma film deposition (10). Consistent with this view is the absence of magnesium in the spectrum of the treated powder. The aluminum atoms or ions are incorporated in the first 5 nm of the plasma polymer film (11).



**Figure 4.** SIMS data of single-layer, pyrrole-coated alumina nanoparticles.

For the double layer coatings of pyrrole (first layer) and HMDSO (second layer), peaks at  $-75$  m/z and  $-89$  m/z in Figure 5 indicate siloxane on the sample surface. The peak at  $-60$  m/z is believed to be the  $\text{SiO}_2^-$  in this figure. However, in the HREM images of the doubly coated samples, we cannot find a distinctive interface between the first and the second polymer layers. The reason is that these two polymers did not crystallize during the plasma synthesis and HREM cannot distinguish these two different amorphous layers.

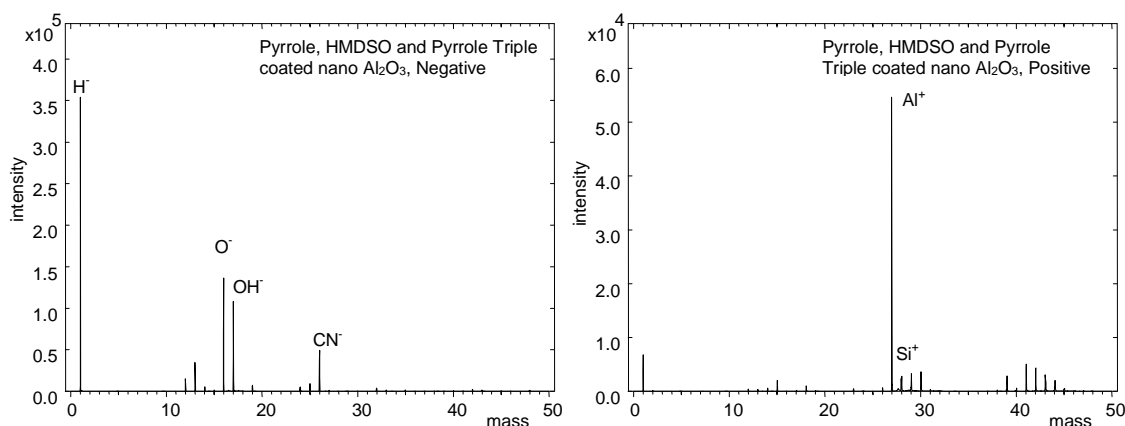
For the triple layer coating, pyrrole was again used to deposit on the surface of second layer of HMDSO. The typical intensity peak at  $-26$  m/z ( $\text{CN}^-$ ) can be found in Figure 6 that confirms the existence of nitrogen-containing molecules. Also the typical patterns of polymerized pyrrole re-appear in Figure 6, and the siloxane peaks have vanished due to the third layer coating. The pattern of pyrrole peaks is similar to that in Figure 4. This indicates that the pyrrole film as the third coating has completely covered the second layer of the nanoparticles.



**Figure 5.** SIMS data of second-layer, HMDSO-coated alumina nanoparticles.

During coating, the polymer is introduced as a vapor and the collision frequency increases with the gas pressure. The rate of polymer condensation on the nanoparticle surfaces may be influenced by many parameters such as electron density, temperature,

and energy density. To achieve a thin and uniform coating on such small nanoparticles, all these synthesis parameters must be optimized. Although a systematic study on the optimization of synthesis parameters has not yet been carried out, the preliminary experimental data have indicated that the coating polymer must be stable and not reactive with the substrate during coating. The gas pressure must be moderate for a low collision rate on the nanoparticle surfaces. In addition, polymerization should take place relatively fast after the condensation on the particle surfaces. These will ensure a uniform coating on the order of 1-2 nm for all particle sizes.



**Figure 6.** SIMS data of third-layer, pyrrole-coated alumina nanoparticles.

In summary, we have coated alumina nanoparticles with multi-layers of pyrrole HMDSO by means of a plasma polymerization treatment. The coating is not only uniform on all particle sizes, but also deposited in an extremely thin thickness of 1-2 nm. Such coating characteristics are essential in establishing multi-layer nanostructures, tailoring unique physical properties, and pioneering novel synthesis route.

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