

Plasma deposition and characterization of acrylic acid thin film on ZnO nanoparticles

Donglu Shi and Peng He

*Department of Materials Science and Engineering, University of Cincinnati,
Cincinnati, Ohio 45221-0012*

Jie Lian and Lumin Wang

*Department of Nuclear Engineering and Radiological Science, University of Michigan,
Ann Arbor, Michigan 48109*

Wim J. van Ooij

*Department of Materials Science and Engineering, University of Cincinnati,
Cincinnati, Ohio 45221-0012*

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Acrylic acid polymer thin films were deposited on the surfaces of nanoparticles of ZnO using a plasma polymerization treatment. The average size of nanoparticles was on the order of 50 nm in irregular shapes. High-resolution transmission electron microscopy (HRTEM) experiments showed that an extremely thin film of the acrylic acid layer (15 nm) was uniformly deposited on the surfaces of the nanoparticles. The HRTEM results were confirmed by time-of-flight secondary ion mass spectroscopy. The effect of plasma power on the polyacrylic thin film was studied by Fourier transform infrared experiments. The deposition mechanisms and the effects of plasma treatment parameters are discussed.

I. INTRODUCTION

Plasma treatment is currently used in surface and interface engineering for improving adhesion, hydrophobicity, hydrophilicity, printability, corrosion resistance, selectivity, or for surface etching or cleaning.¹⁻³ The main principle of the plasma technique is that the ionized and excited molecular radicals created by the electrical field bombard and react on the surface of the substrate. These ions and radicals may etch, sputter, or deposit on the substrate surface. As a result, the surface properties of substrates are modified. The plasma technique is a room-temperature and environmentally benign process. Due to these characteristics, the plasma technique can be used for surface modification and thin film deposition on almost all substrates, including metal and alloy plates, polymer films, paper, glass, porous materials, and particulate matter.

In current research of nanomaterials, it has become critical to modify the surfaces of the nanoparticles for both fundamental research and engineering applications.⁴⁻¹⁰ In our previous work, the modification of nanoparticle surfaces involved deposition of ultrathin films (1-5 nm) on the nanoparticles by plasma treatment.¹¹⁻¹⁴ The deposited film was not only uniform but also tailored to multilayers for developing unique nanostructures. This novel nanotechnology is of particular importance in

electronics, functional devices, new material synthesis, nanobiomolecular applications, tissue engineering, and drug delivery. One of the possible applications of nanocoating is in ion exchange for removing metal ions from water. If on the surface of these nanoparticles, an extremely thin layer of polyacrylic film can be coated by a plasma treatment, the polyacrylic film will react with metallic ions in water. As a result of the high surface-to-volume ratio of these nanoparticles, the efficiency of ion exchange in the water flux is much higher than that of other types of traditional reactors. After coating, it can be tested for capacity and affinity, initially by mixing the powders with solutions of suitable cations or anions, such as Cu^{2+} , H_2AsO_3^- , etc. The reduction in concentration of the ions can be measured by atomic absorption spectroscopy (AAS) and inductively coupled plasma (ICP) techniques, depending on the ion. The change in pH is also an indication of the amount adsorbed as the active functional groups are initially in the $-\text{COOH}$ or $-\text{NH}_2$ form. However, in this study we shall only focus on the coating of the nano ZnO with acrylic acid (AA) films.

For nanoscale ceramics particles, the challenge is whether they can be well dispersed in space; further, in a well-dispersed condition, if 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 address these issues and report experimental

results on the deposition of AA polymer ultrathin films on the surfaces of nanoscale ZnO particles by a plasma polymerization process.

II. EXPERIMENTAL

It has been difficult to deposit thin films on nanoparticles in the plasma polymerization process due to severe aggregation and large surface area per unit mass of the particle.^{15–17} In the plasma thin film deposition process, it is necessary to expose the surface of the nanoparticles to the plasma. The unexposed regions of the nanoparticles are hardly modified. The fluidized bed reactor is an ideal tool for gas–particle reactions due to the intensive mass and heat transfer between the two phases, short reaction time, and flat temperature profile.^{15–17} Therefore, the combination of plasma polymerization and the fluidized bed process represent an innovative approach for low-temperature surface modification of nanoparticles.

The plasma-coating facility is a homemade system. The schematic diagram of the plasma reactor for thin film deposition of nanoparticles is shown in Fig. 1. It consists mainly of a radio frequency (rf) source, the glass vacuum chamber, and pressure gauge. The vacuum chamber of plasma reactor has a long Pyrex® glass column about 80 cm in height and 6 cm in internal diameter.^{15–17} The powder is placed on the fluidized bed and stirred mechanically. As the powder is being fluidized, they are charged in the rf zone. Inlet gas carrier as shown in Fig. 1 introduces the monomers. Using this system, the properties of a variety of powders can be modified quite effectively. In our previous work, powders treated included

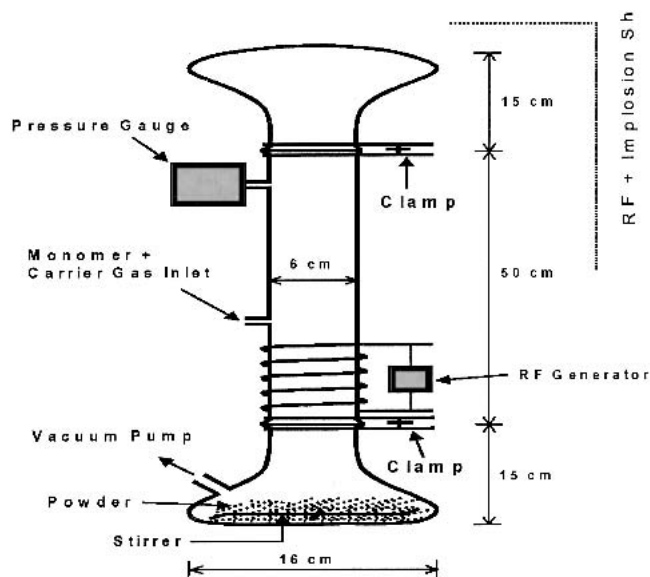
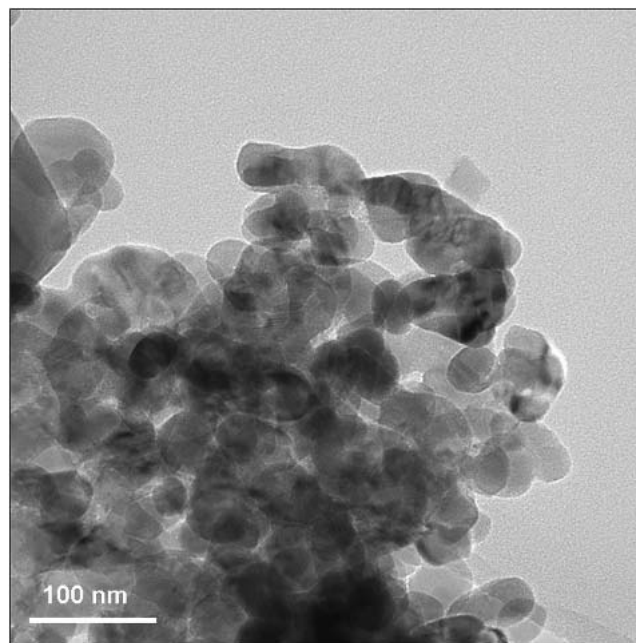
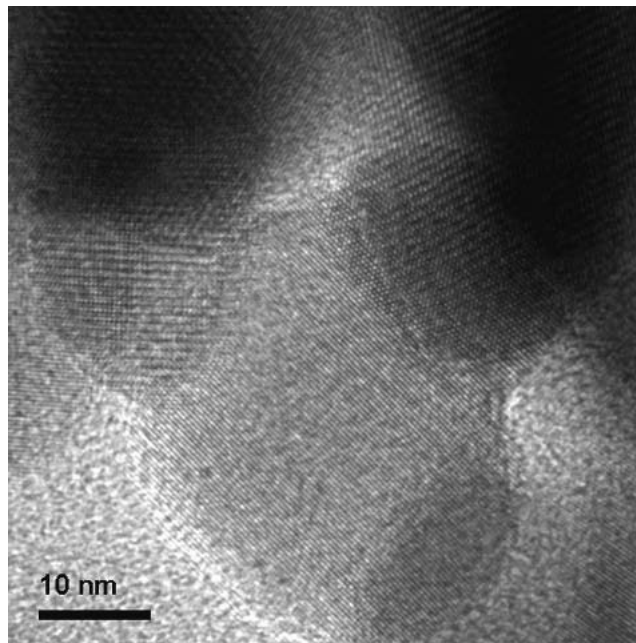


FIG. 1. Schematic diagram of the plasma reactor for thin polymer film coating of the nanoparticles.

silica, talc, mica, cerium sulfide (pigment), boron nitride, lactose, iron oxide, chromium oxide, and others. It was demonstrated that water-soluble powders could be made sparingly soluble or slowly dissolving in water. Monomers that were used included hexamethyldisiloxane (HMDS), acrylic acid, acetylene, pyrrole, and perfluorohexane (PFH).



(a)



(b)

FIG. 2. (a) Bright-field image of the original, uncoated ZnO nanoparticles; a particle size distribution ranging from 10–50 nm. (b) HRTEM images of the original ZnO nanoparticles showing crystal lattice and the uncoated nature of the nanoparticle surfaces.

In this experiment, we selected nanoscale ZnO particles of 50 nm. The nanoparticles of ZnO are vigorously stirred at the bottom of the tube, and thus the surface 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. AA was used as a monomer 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 g powder were treated.

After the plasma treatment, the nanoparticles of alumina were examined by 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 experiments were performed on a JEM 4000EX TEM. The TOFSIMS analyses were performed on an ION-TOF Model IV instrument. In the Fourier transform infrared (FTIR) experiment, potassium bromide (KBr) of 99%+ purity was obtained from Aldrich Chemical Company Inc. (Milwaukee, WI). The coated powder was mixed with KBr and pressed into small pellets for the FTIR experiment. FTIR spectra were acquired on a BIO-RAD FTS-40 FTIR spectrometer with a BIO-RAD transmittance attachment.

III. RESULTS AND DISCUSSION

In transmission electron microscopy, the original and coated ZnO nanoparticles were dispersed onto the carbon film supported by Cu-grids for the TEM operated at

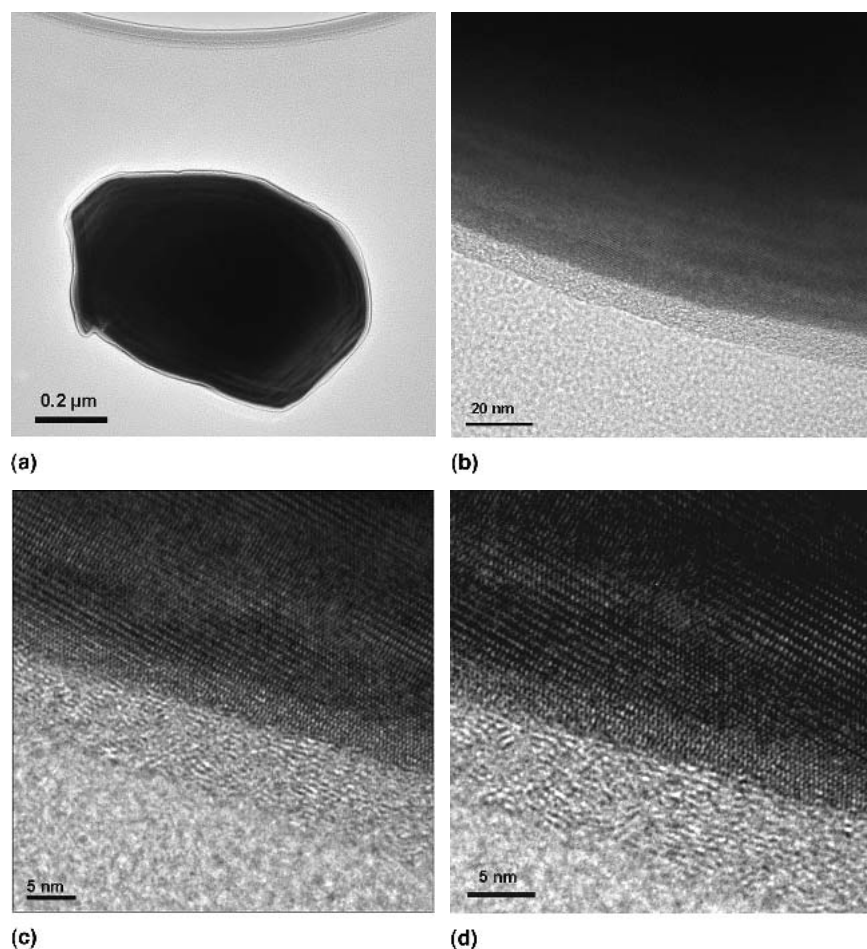


FIG. 3. (a) Bright-field TEM image of the AA-coated ZnO nanoparticles at low magnification. (b) HRTEM image showing the AA-coated ZnO nanoparticle surfaces at higher magnification. (c,d) HRTEM images of AA-coated ZnO showing the amorphous nature of the AA thin film and the crystal lattices of the ZnO structure.

200 kV. Figure 2(a) shows the TEM image of the original, uncoated ZnO nanoparticles. As can be seen in this figure, the average particle size is about 50 nm. These particles also exhibit the irregular shapes for all sizes. Figure 2(b) is the high-resolution image of the original ZnO nanoparticles. The lattice image further reveals the crystallographic features of the naked ZnO particles. The smaller particles have a size on the order of only 15 nm. Figures 3(a)–3(d) are the bright-field images of the coated ZnO nanoparticles at different magnifications. Figure 3(a) shows the low-magnification of a ZnO particle coated with AA film. As can be seen, the coating

is uniform all the way around the entire surface of the particle. In our TEM observation we found that, although these particles have different diameters, the film remains the same thickness indicating a uniform distribution of active radicals in the plasma chamber. Figure 3(b) is an image of a higher magnification. The uniformity of the AA thin film can be clearly seen in this photograph. The film thickness is about 5 nm. Figures 3(c) and 3(d) are images at even higher magnifications. From these images, the film was identified as typical amorphous structure by high-resolution electromicroscopy observation over different particles. The lattice image of ZnO forms a clear contrast with the amorphous AA film at the interfaces.

To confirm the TEM observations shown in Figs. 2 and 3, TOFSIMS was carried out to study the surface films of the nanoparticles. Figures 4(a) and 4(b) show parts of the TOFSIMS spectra of coated nanoparticles of ZnO. One can see that the coated ZnO has strong peaks of $C_2H_4^+$, $C_2H_5^+$, OH^- , CH_2^- that indicate the surface coating of the nanoparticles and are consistent with the high-resolution TEM (HRTEM) data presented in Figs. 2 and 3. The coated ZnO particles show the typical characteristic cluster pattern of plasma-polymerized polyacrylic film.

FTIR was used to study the effect of plasma power on the structure of the AA films. The concept of the ion exchange is illustrated in Fig. 5. The COOH function group in the coating can be used to react with ions in water as indicated in this figure. More functional groups are desired in the coating films for an effective ion exchange process. However, we found that the number of function groups will decrease as the plasma power increases. At low powers, on the other hand, not enough cross linking will exist to keep the film insoluble. Therefore, the plasma polymerization power must be optimized.

Figure 6 shows the FTIR spectrum of AA coated nano-clusters of ZnO. As can be seen in Fig. 6(a), the strong C=O peak near 1700 cm^{-1} indicates the surface coating of the nanoparticles, and it is consistent with the HRTEM data presented in Fig. 3. The peak of C=O intensifies as the plasma power increases up to 80 W, indicating a strong plasma power dependence. The intensification of this peak also indicates an increased amount of

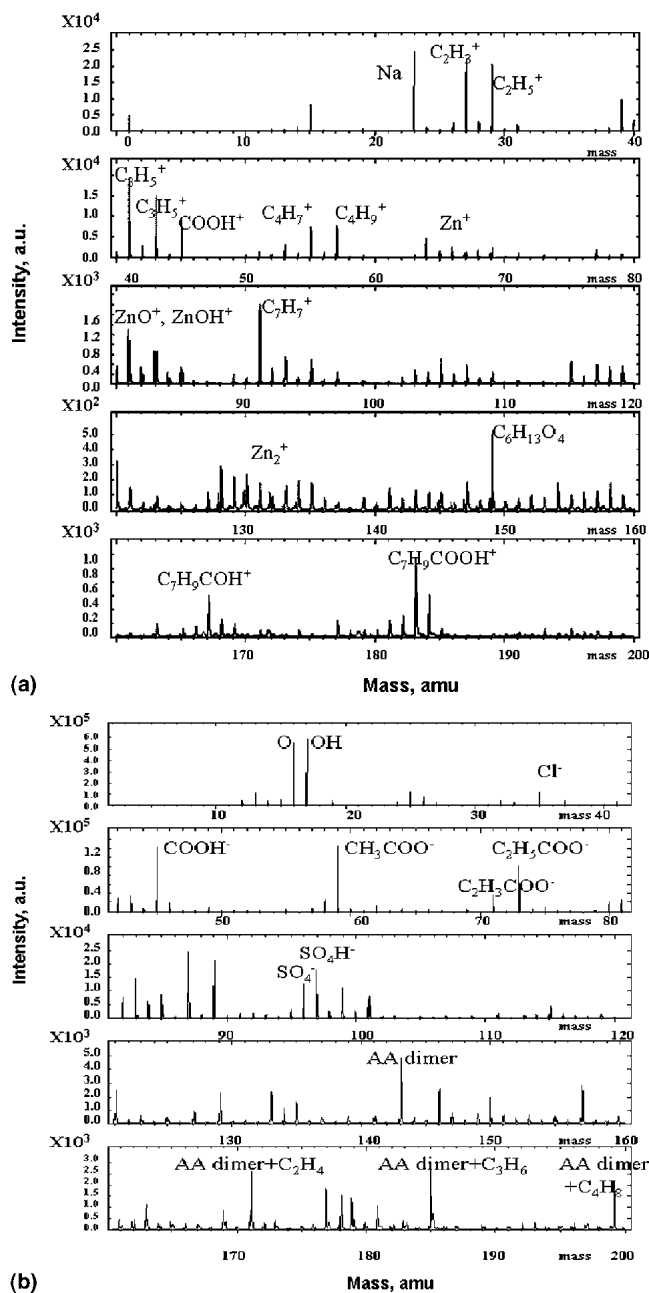


FIG. 4. TOFSIMS spectra of the AA-coated nanoparticles of ZnO.

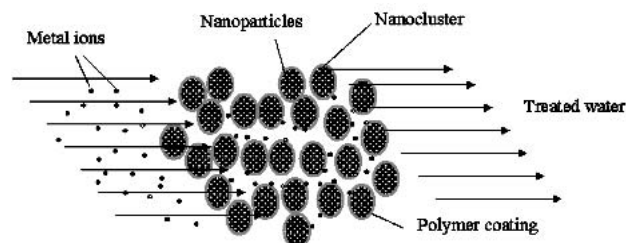


FIG. 5. Schematic diagram showing the concept of ion exchange due to AA thin film on the nanoparticle surface.

functional group of C=O that is needed for ion exchange. To investigate the film solubility in water, we immersed AA-coated powder in the Ni⁺ solution. After 1 h, the sample was removed from the solution, dried, and the FTIR experiment was again performed on the nickel solution treated powder. The results are shown in Fig. 6(b). In this figure we can see that the AA film is entirely soluble when the plasma power was 15 W and 39 W. The FTIR spectra clearly show that the film was removed by the nickel solution after immersing for only 1 h. However as the plasma power was increased to 60 W [Fig. 6(c)] and 80 W [Fig. 6(d)], the AA film remained after immersion in the nickel solution. This indicates that large cross links exist in the polymer, which prevented the AA film from dissolving in the nickel solution; even the polymer has the strong hydrophilic function groups of COOH.

Vollath and Szabo reported polymer coating of polymethyl methacrylate on Fe₂O₃ particles using a microwave plasma synthesis technique.¹⁸ In their experiment, the monomer condensed at the surface of the particles and polymerized under the influence of the ultraviolet radiation generated by the microwave plasma used to create the iron oxide particles. However, in their process, the coating polymer occupied about 80 vol% of the coated particles. Therefore, the experiment should not be described as coating, but rather as an embedment of ceramic cores in the matrix of a polymer matrix. In contrast, in our experiment as shown in Figs. 2 and 3, a uniform thin film of polymer was successfully deposited uniformly onto the surfaces of the nanoparticles. This thin, uniform coating is also ensured on particles of all sizes as evidenced in these figures. It should be noted

that such a thin, uniform coating of the nanoparticle surface is essential in some of the cutting-edge applications. For instance, in some applications the overall electrical conductivity has to be enhanced by coating a conducting layer on nanoparticles. The electron charges must be mainly transported through the coated particle surfaces. Obviously, a thick, high-volume “coating” will not serve this purpose. On the other hand, several other applications would require multiple layer coatings, and each layer would be on the order of a few nanometers. Only the coating method described here can ensure such a fine nanostructure with several layers.

Based on the data provided by McHale *et al.*,¹⁹ the surface energy of γ -Al₂O₃ can reach the order of 30 kJ/mol for a particle size less than 10 nm. For such a high surface energy, the nanoparticles would naturally agglomerate under the normal conditions. However, in the plasma state, the nanoparticles experience plasma oscillations. Plasma is a medium with equal concentration of positive and negative charges. In a solid, the electrons are balanced by the ion cores. At a specific plasma frequency for a longitudinal plasma oscillation, for example, the electrons are displaced uniformly relative to the positive ion cores. As both of them are evenly overlapped, the solid is electrically neutral. However, as the electrons are uniformly displaced by a small distance x from the ion cores, this displacement establishes a surface charge density σ ($= nex$; n , electron density; e , electron charge) on one side of the solid. An electric field, E ($= 4\pi\sigma$) is produced in the solid. This field tends to restore the electrons to their equilibrium positions. Due to this plasma oscillation, the surface charges of the particles constantly change their signs, producing an alternating repulsive

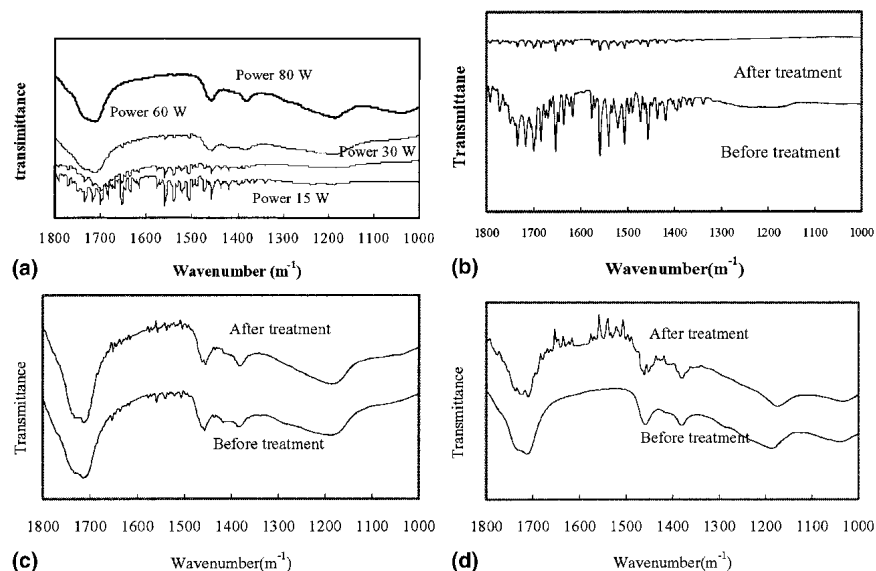


FIG. 6. (a) FTIR spectra of as AA-coated ZnO at different plasma powers. The FTIR spectra of Ni solution treated, AA-coated ZnO nanoparticles at plasma power of (b) 15 W, (c) 30 W, and (d) 80 W.

force between the particles. Therefore, in the process of fluidization, the nanoparticles are well dispersed in the reactor.

It is well known that a growing film of a plasma polymer on a substrate is continually bombarded by positive ions.²⁰ If the plasma also contains an organic monomer, these ions are primarily hydrogen ions (protons). The protons attach themselves to the film. The film is thus positively charged most of the time. In the case studied in this paper, the substrate consists of nanosize powders in a fluidized bed. The positive charges developed on the powder particles will keep them well dispersed in the plasma, making them accessible to the organic radicals that are responsible for the film growth.²⁰ This simple mechanism explains why plasma polymerization of fine particles in a fluidized bed is so effective.

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.

V. CONCLUSION

In conclusion, we successfully deposited polyacrylic thin films on ZnO nanoparticles by using plasma polymerization. The HRTEM experiments showed uniform coatings on irregularly shaped ZnO particles with an average thickness of 5 nm. TOFSIMS experimental results confirmed the deposited film to be polyacrylic acid polymer. The effect of plasma power on the structure of the polyacrylic film was studied by FTIR experiments. The plasma power dependence indicated that the cross-links were enhanced at higher powers. Above 60 W, the polyacrylic film remained insoluble. The deposition mechanism was discussed based on the surface behavior of nanoparticles.

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