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## ADP011018

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This paper is part of the following report:

TITLE: Materials Research Society Symposium Proceedings Volume 635. Anisotropic Nanoparticles - Synthesis, Characterization and Applications

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ADP011010 thru ADP011040

Mat. Res. Soc. Symp. Proc. Vol. 635 © 2001 Materials Research Society

# Nanoparticles and Nanocomposites in RF Plasma

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## ABSTRACT

The use of low pressure radio-frequency (rf) plasma for nanoparticle formation and the deposition of thin film on particulate substrates are reported. Plasma polymer particles are synthesized in a capacitively-coupled Ar/monomer discharge at rf power of 15-30 W. A variety of particle structures are observed, including monodispersed nanospheres and liquid-like viscous nano-droplets. Styrene in particular is observed to produce hollow nanospheres. By manipulating the process parameters, films of plasma polymers can be deposited onto suspended submicron particles. We take advantage of the electrostatic trapping of "dusty plasma" to suspend small particles in plasma for extended periods of time until the desired coating thickness is achieved. Sub-micron silica particles introduced into a low pressure rf Ar/monomer plasma are coated with film of thickness ranging from 2 to 70 nm.

## INTRODUCTION

Most efforts in gas phase thin film deposition have been directed towards flat substrates. While it is very difficult to apply a homogeneous and low-thickness coating to particles by physico-chemical or purely chemical approaches such as spraying, dipping, or fluidization [1], polymer films as thin as several tens of angstroms can be deposited in plasmas [2]. High molecular weight solid deposits formed in plasma are termed "plasma polymers." High energy electrons in plasma sever chemical bonds and ionize neutral species, making the polymerization process atomic in nature. The final product can be controlled via process parameters [3], and materials with many unique and useful features have been obtained [4-11]. Almost any compound that can be brought into the plasma can undergo polymerization. This leads to a wide variety of products not observed from thermally activated reactions. Plasma polymers are generally highly cross-linked and can therefore deposit as pinhole free film. Plasma polymers also deposit in the form of particles depending on the monomer and reaction conditions [12, 13], giving even more varieties in plasma polymer coating. However, only film deposition of plasma polymerization has been extensively studied thus far. This work reports our study of the particle formation during plasma polymerization, since these particles may be used as substrates for the coated nanocomposites of our interest.

The key to thin film deposition on particles in plasma is a controlled manner of fluidization of the substrates. The present work demonstrates the new concept of fluidizing particles using "dusty plasma," i.e., plasma with trapped particles, for surface coating. We have successfully fabricated nanocomposites with a silica core and plasma polymer coating using this method. There have been only very few efforts of thin film deposition on particles in plasma to date[1, 14, 15]. In those cases, either a tumbling device was used to keep the particles separated or a flow system was used where it was difficult to control the residence time of the particles entrained. In our system, these problems are easily solved using particle trapping.

## EXPERIMENTAL

The reactions are carried out in a capacitively-coupled rf plasma at 13.56 MHz. The operating pressure is between 10 mTorr and 1 Torr. In such a "cold plasma," electrons and ions are not in thermal equilibrium, with electron temperature typically at about 2-3 eV and ions slightly above room temperature, and an ionization fraction under 1% [16]. Figure 1 is a schematic representation of the reactor used in our work. The parallel-plate electrodes, separated at 1-2 cm, are different in size—the grounded upper electrode 8 cm in diameter and the powered lower electrode 4 cm—to produce an asymmetric plasma with a large negative dc bias across the lower sheath where most particles are trapped. Small particles introduced into plasma quickly charge up, and the equilibrium charge is negative due to the large difference in electron and ion mobility. These particles experience a variety of forces [17]. Electric and ion drag forces dominate for submicron particles, and electric and gravitational forces dominate for above-micron particles [18]. The particles become trapped at parts of the plasma where the net force vanishes. For smaller particles, this occurs in the bulk plasma, while larger ones are suspended near the sheath/plasma boundary or inside the sheath, as seen in figure 2, a snapshot of the particle trapping phenomenon in our reactor. The lower electrode has a slightly depressed center of 2 cm in diameter to provide horizontal confinement of the trapped particles. A laser is used to illuminate the particle clouds for visualization with a CCD camera.

Upon opening the reservoir, particles to be coated fall directly into the interelectrode plasma region through the hollow upper electrode. A fine mesh at the entry point eliminates large agglomerates. The particle substrates used in this work are spherical silica particles in the size range of 0.5-1.5 μm. The particles remain suspended in the plasma throughout the reaction, and fall onto the lower electrode as the discharge is extinguished. Ar is used as the carrier gas, and monomers studied are styrene, isopropanol, and ethylene. A carrier gas is needed in most cases because the pulsation of a pure monomer plasma resulting from the polymerization process easily disturbs the trapped particles.

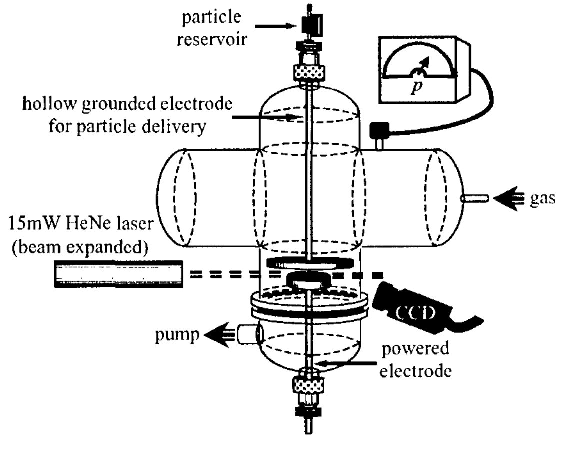


***Figure 1.** A schematic representation of the glass plasma reactor used in our work.*

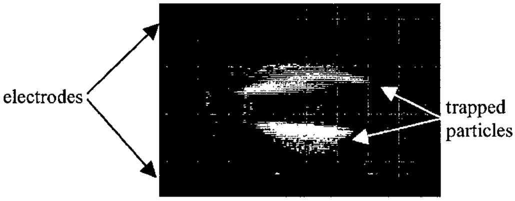


*Figure 2. Particles trapped in an rf plasma in our reactor.*

# RESULTS AND DISCUSSIONS

## Particle formation of plasma polymer

Plasma polymer can deposit either as film or particles. The three monomers studied have different tendency to form particles. Styrene plasma polymer mostly deposits as particles. Isopropanol polymerizes into particles and film with comparable ease. Film is almost the exclusive product of the plasma polymerization of ethylene. A wide variety of interesting particle morphologies are observed in the reaction products.

The plasma polymer of styrene readily deposits as spherical particles at 15W of rf power, 400 mTorr of system pressure, and 4:1 Ar:styrene flow rate. TEM images like figure 3a suggest that the particles have an empty core. Figure 3b is a micrograph of a 30nm- section of the resin dispersed with these hollow particles, providing better core and shell contrast. The particles are mostly hollow and spherical, and range from 50-300 nm in diameter. The size of core is about a quarter to a third of the particle diameter. These particles are amorphous as determined by electron diffraction.

The TEM image of one particle in figure 3a is analyzed by plotting the pixel intensity vs. the distance from the center of the particle as shown in figure 4. The intensity is directly proportional to the incident electron flux. It is evident from figure 4 that the mass thickness of the particle center is much smaller than would be expected of a solid sphere. The significance of this result is that if the particle consists of a spherical core and shell, the minimum intensity corresponds to the boundary of the two layers. As shown in figure 4, the experimental data can

(*a*) (*b*) (*c*) (*d*)

***Figure 3****. TEM micrograph of* (*a*)*hollow particles of styrene plasma polymer made at 400 mTorr*; (*b*)*a 30nm-section of the resin dispersed with the hollow particles in* (*a*); (*c*)*broken shells of styrene plasma polymer made at 40 mTorr*; (*d*)*monodispersed nanospheres of styrene plasma polymer made at 28mTorr.*

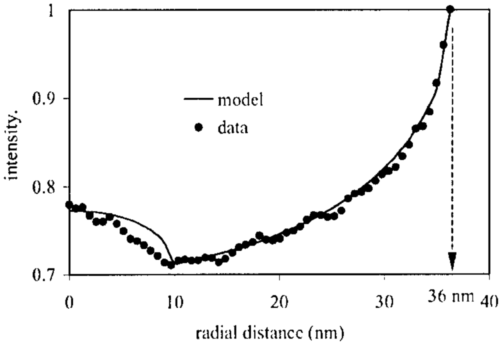


***Figure 4.*** *Radial intensity profile of a hollow styrene plasma polymer particle (intensity normalized to background). The particle radius is 36 nm with a core radius of 10 nm. The Beer-Bouguer model assumes an empty core but constant absorption coefficients.*

be described by a simple Beer-Bouguer type of model

$$\Phi = \Phi_0 e^{(-\alpha_s x_s - \alpha_c x_c)} \qquad (1)$$

where $\Phi$ is the electron flux that go through the sample, $\Phi_0$ the initial electron flux, $\alpha$ the absorption coefficient of the sample, $x$ the thickness of the sample, and the subscripts $s$ and $c$ stand for shell and core. In this case, the particle radius is 36 nm, the core radius is 10 nm, $\alpha_s$ = 0.00485, and $\alpha_c$ = 0, meaning an empty core. The mechanism of hollow particle formation is under investigation. The morphology is not restricted to hollow spheres only. Under similar reaction conditions but a lower system pressure, broken shells are observed (figure 3c). Monodispersed spheres of about 40nm (figure 3d) are also observed at styrene pressure of 28 mTorr and no Ar flow.

Isopropanol does not form hollow plasma polymer particles. Instead, monodispersed spheres of about 35nm are found at 30W rf power, 600 mTorr total system pressure, and 3:1 Ar:isopropanol flow rate. Also obtained under the same conditions are structures that resemble highly viscous droplets in the high nanometer range (figure 5).

## Plasma polymer thin film deposition on particulate substrates

Spherical silica particles in the high nm and low μm size range have been successfully coated with plasma polymer of all three monomers. Film as thin as 2nm has been deposited on

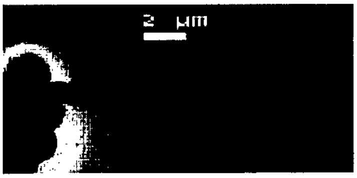


***Figure 5.*** *TEM micrograph of plasma polymer beads of isopropanol made at 30W, 600mTorr, 3:1 Ar:monomer flow*

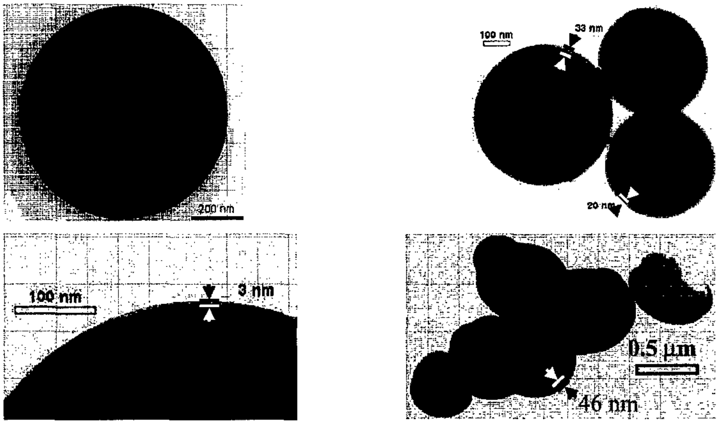
the substrates. The nanocomposite is observed under TEM where the plasma polymer film and the bulk silica particle have different contrasts. The micrographs in figure 6 show comparisons of uncoated and coated silica particles. Energy dispersive spectroscopy (EDS) verifies that they are silica particles.

Although the film thickness varies among particles and sometimes is even non-uniform on the same particle, the trend can be observed that a longer deposition time leads to thicker film, as illustrated in figures 6c and 6d of silica particles coated with the plasma polymer film of isopropanol for different lengths of time. The estimated power deposition per unit pressure of monomer for figure 6d is four times greater than that for figure 6b. Thicker film is deposited in the former case in just half of the reaction time. Therefore, qualitatively, higher power density absorbed by the monomer leads to greater deposition rate.

Ethylene plasma polymer deposits as film as well on silica particles (figure 7a), while styrene plasma polymer deposits as both film and particulates on the silica particle surface (figures 7b-d). Film deposition of styrene plasma polymer is observed to increase at lower pressures. This is also seen in the particle coating experiments with styrene. The pressure for figure 7b is much lower than for that for figure 7c. The particle in figure 7b is coated with a film, whereas the particle in figure 7c is coated with both film and particulates. This is most likely due to the decreased monomer concentration in the gas phase at lower pressures which facilitates film formation [11].

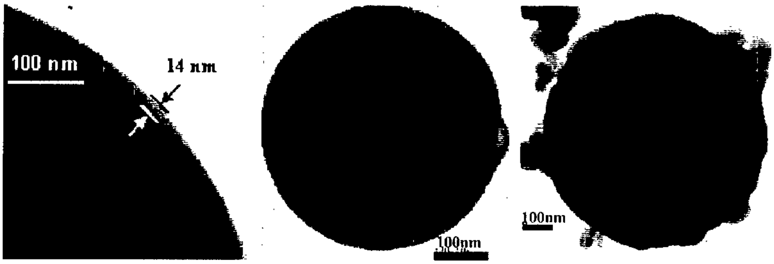
## CONCLUSIONS

We have successfully proved the concept of plasma polymer coating of nano/micro-particles using the principle of "dusty plasma." Film as thin as 2nm has been observed on the particles



(c) (d)

***Figure 6.*** *TEM micrographs of (a)an uncoated silica particle; (b) silica particles coated with plasma polymer film of isopropanol for 20 min. at 30W of rf power, 800 mTorr of system pressure, and 1:1 Ar:isopropanol flow rate; (c)a silica particle coated with plasma polymer film of isopropanol for 5 min. at 30W of rf power, 200 mTorr of system pressure, and 1:1 Ar:isopropanol flow rate; (d)same conditions as (c) for 10 min.*



(*a*) (*b*) (*c*)

***Figure** 7. TEM micrographs of silica particles coated with (a)ethylene plasma polymer at 20W, 100 mTorr, and 1:1 Ar:ethylene flow rate; (b)styrene plasma polymer at 15W, 28 mTorr, and no Ar flow; (c)styrene plasma polymer at 15W, 470 mTorr, and 6:1 Ar:styrene flow rate.*

under TEM. The coating thickness can be controlled through deposition time. The film, however, is not always uniform among the particles or on the same particle. It has been shown that styrene plasma polymer readily deposits as hollow nanoparticles. Other morphologies are also observed in the plasma polymer of styrene as well as isopropanol and ethylene.

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