

# Thin-Film Deposition on Nanoparticles in Low-Pressure Plasma

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## ABSTRACT

We have synthesized hollow nanoparticles by a two-step process: a particle that acts as a template is coated with amorphous hydrogenated carbon in a low pressure plasma. The core particle is then dissolved to produce a hollow nanoshell. Transmission electron microscopy (TEM) images depict the thickness and the uniformity of the adherent polymer coatings. In order to determine the permeability of the shell, coated KCl particles are dissolved in water and the conductivity of the solution is measured as a function of time. These nanoshells exhibit a delayed release response which can be controlled via the deposition time of the film.

**Keywords:** Plasma polymerization, Hollow nanoparticles, Controlled release

## 1 INTRODUCTION

Because of their physical and chemical properties, nanoparticles are used in a variety of applications that range from biomedical [1],[2],[3], to optical [4],[5], to electronic fields [5]. By depositing thin films onto the particle surface it is possible to enhance the optical, mechanical, thermal, and electrical properties that are unattainable in the particles alone. Silica nanoparticles are one of the highly attractive nanostructures for a wide variety of nanotechnology applications such as catalysis, adsorption, separation, and sensing [7]. In addition to the coating process that improves the surface properties of nanoparticles, they can be used to improve the performances of organic polymers [8],[9]. By mixing the inorganic particles specially silica with polymers organic/inorganic composites form which has the rigidity and thermal stability of inorganic materials and the flexibility and ductility of organic polymers. Various synthesis routes can prepare the so-called nanocomposite structures as Hajji et al. reported [10]. Sol-gel, blending, and in situ polymerization are the general processing techniques to produce polymer/silica nanocomposites [9]. In addition to these methods, plasma deposition technique is another approach for a wide range of materials in order to modify their surfaces and also to fabricate nanocomposites.

Plasma enhanced chemical vapor deposition, PECVD, is a technique that modifies nanoparticles by coating them with a solid produced by the plasma decomposition of an organic (usually hydrocarbon) molecule. Such solids are often referred to as plasma polymers. This process offers a number of advantages that are not possible with colloidal processing: (1) the precursor used in plasma may not contain the type of functional groups normally associated with conventional polymerization; (2) Very uniform thin films from few nm to more than 1  $\mu\text{m}$  can be formed and the thickness can be easily controlled via the deposition time; (3) Because of the cross-linked structure, the polymer film is mechanically and chemically stable [11],[12]. By taking advantage of these properties we tailored plasma polymer coating process to produce hollow nanoparticles.

Hollow particles are of great interest for the encapsulation of materials such as drugs, dyes and cosmetics in order to release them controllably over the time [13],[14]. These are commonly produced by a two-step process that starts with the coating the surfaces of templates with a desirable thickness, followed by a chemical dissolution or calcination of the template. This synthesis process has been employed for variety of materials including ceramics, polymers, and metals [15]. In some cases, core removal through the polymer shell is so slow because of the low diffusion in the small pores of the shell, <10 nm. In this case, mesoporous polymer capsules are used to accelerate the core removal process [16],[17]. Here we report the preparation of plasma polymer hollow particles after a successful selective core dissolution process which proves the permeability of the shell.

In our previous work we developed a plasma based process for depositing plasma polymers of various thicknesses onto micro- and nanoparticles [18]. Here we show that these films can be used to produce hollow particles (nanoshells) via chemical etching of the template particle. In this paper we describe the fabrication of the hollow particles and present experimental results that reveal their permeability characteristics.

## 2 EXPERIMENTAL PROCEDURE

Deposition process in order to coat nanoparticles takes place in two different plasma reactors one with two par-

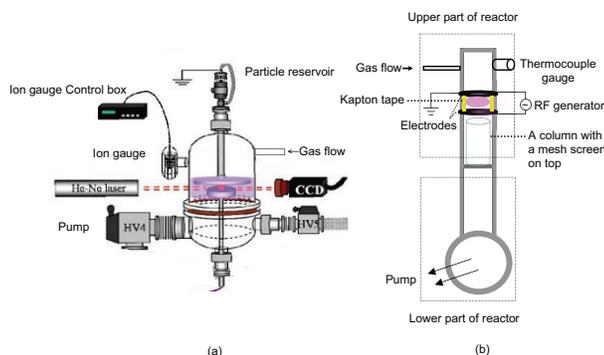


Figure 1: Schematic of the reaction setup: (a) a classic semi-batch reactor, (b) a novel tubular reactor.

allel electrodes, and one with two external ring electrodes. A schematic of the reaction setup is shown in figure 1. The major part of the setup is a pyrex reactor that allows a full visual access to the coating process. The total volume of the chamber is 1.5 liter while the plasma glow occupies approximately 0.5 liter in volume between the two electrodes. Adjustable stainless steel electrodes are spaced apart by a distance of 0.5 cm to 5 cm. The lower electrode, 4 cm in diameter, is powered and the upper electrode, 8 cm in diameter, is grounded. Both electrodes are capacitively coupled by a radio frequency (RF) power supplier at 13.56 MHz and operates in the pressure range 100 mtorr to 1000 mtorr. Two pumps, a roughing pump and a diffusion pump, are connected to the gas outlet for evacuating gases from the chamber. During operation, the precursor vapor and Ar gas enter the chamber via the gas inlet pipe. The particles are introduced into the chamber as a dry powder after pressing through a set of mesh screens. These particles acquire a charge as they fall through the plasma and become trapped in the sheath region above the bottom electrode where they remain over extended periods of time. A beam-expanded 14 mW HeNe laser illuminates the trapped particles and a charge coupled device (CCD) camera is used to capture the process. When the plasma is turned off, particles are collected from the surface of the lower electrode.

Since particles are suspended, this reactor leads to the formation of coatings with a high degree of radial uniformity. However, the amount of particles that can be processed is very small and limited by the volume of the sheath space. The second reactor was designed to circumvent this difficulty. The reactor operates with the same RF power, 10-150 W at 13.56 MHz, which is applied to the external electrodes, and is attached to the same vacuum system which we used for the parallel-plate reactor. Particles are placed on the wall of the reactor close to the charged electrode by spreading them on the surface of the Kapton tape. Double sided Kapton tape that are suitable for powder coating are used

to carry particles on their surfaces. A set of 100-400 mesh screens are used to press and separate particles on the HN tape. This Kapton tape has silicone adhesive protection and is ideal for powder coating since it does not leave any residue. Through this process we can now treat 0.1-1 g of particles per run. After the deposition process, which typically lasts 1 to 30 min, the particles are removed from the reactor and placed in 5% aqueous HF overnight to dissolve the silica and produce hollow particles. Many other materials can be used as a sacrificial template. In addition to silica we have used KCl, which offers the advantage that its dissolution kinetics can be studied easily with conductivity measurements.

Monodisperse spherical silica particles of 200 nm and 1 $\mu$ m diameter are obtained from Geltech Inc. By using Stober method we also synthesize silica particles as small as 20 nm diameter in our laboratory. In order to eliminate the moisture of particles, they should be alcohol washed and oven dried prior to inserting them into the reactors. KCl particles are prepared in our lab by using a constant output atomizer (model 3075). Isopropyl alcohol (IPA) is purchased from Sigma-Aldrich and is used as precursor since it produces smooth and well-defined films. The discharge is normally run for 10-40 minutes. When particles are collected either from the electrode or the surface of the Kapton tape, they are placed on TEM support films. The process conditions for this study are 6 sccm of Ar and 0.5 sccm of isopropanol leading to the total pressure of 200-500 mtorr. TEM analysis of the nanoparticles was performed on a Philips EM420T operating at 120 kV. This instrument is equipped with a CCD camera and an X-ray Energy-Dispersive Spectroscopy (EDS).

### 3 RESULT AND DISCUSSION

TEM images of uncoated silica and coated silica particles in plasma are given in figure 2. The size distribution of the bare silica particles are 200 $\pm$ 12 nm. Different film thicknesses can easily be achieved by controlling the plasma processing duration since the average deposition rate is 2.5 $\pm$ 0.5 nm/min. Figure 2 shows silica particles 200 nm in diameter coated with the amorphous hydrogenated carbon (a:H-C) films for 10 minutes.

TEM images of IPA plasma polymer hollow particles are shown in figure 3. The spherical silica particle diameter is 200 $\pm$ 12 nm. The thickness of the film is 50 $\pm$ 10 nm and was obtained after 20 min of deposition. Figure 3a shows a TEM image of the particles after treatment in HF. These images demonstrate that the silica core has completely dissolved while the shells have remain intact. Apparently, the films are chemically inert to the corrosive power of hydrofluoric acid. Moreover, it is apparent that the films are permeable to small molecules since HF, H<sub>2</sub>O, and dissolved silica (aggregates of silicic acid) can all pass through the shell. To obtain quanti-

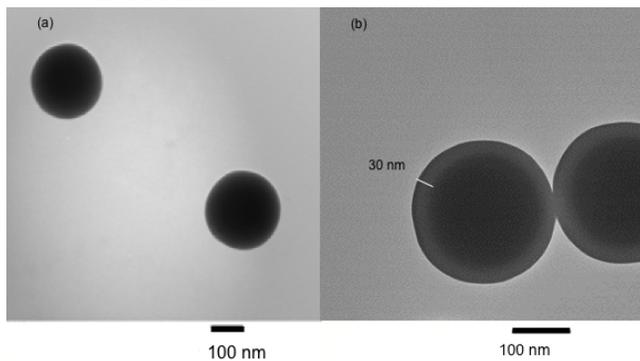


Figure 2: TEM images of: (a) untreated silica particles with diameter of 200 nm, (b) treated silica particles with a plasma coating of 30 nm

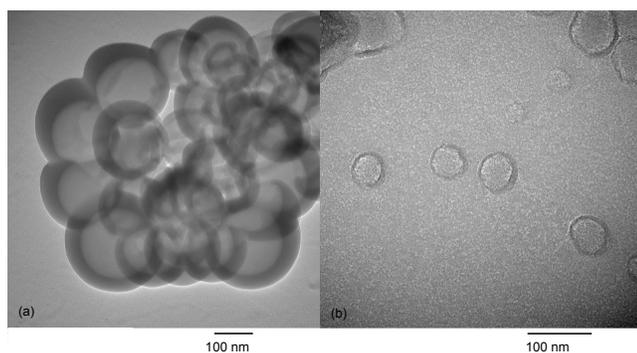


Figure 3: TEM images of: hollow particles after etching (a) silica (b) KCl core

tative information about the permeability of the shells, we switched from silica to potassium chloride. Spherical KCl particles were produced by spray-drying an aqueous solution of the salt. The resulting particles are spherical but not as monodisperse as silica, with sizes in the range 20–100 nm. The fabrication of the hollow particles was similar to that of silica except that the dissolution of the core was accomplished in water. Figure 3b shows the hollow nanoshells after the dissolution of the KCl core.

To measure the concentration of dissolved KCl in water, a conductivity meter (Thermo Orion model 105) is used. The in-vitro release of KCl from the core is illustrated in figure 4. The release profile may be divided into three stages. The first stage is marked by a very rapid increase of conductivity. Within 10 minutes of stirring the coated KCl particles in solution, the conductivity rises to about 72% of its final value. We attribute this increase to uncoated KCl particles and not uniformly coated KCl that are present in the sample. In contrast, for the control the concentration of the uncoated KCl reaches the maximum within the first 82 seconds. The next stage is characterized by a slow, continuous release that lasts over a period of several days. Within the 13 days we observe the slow increase of KCl

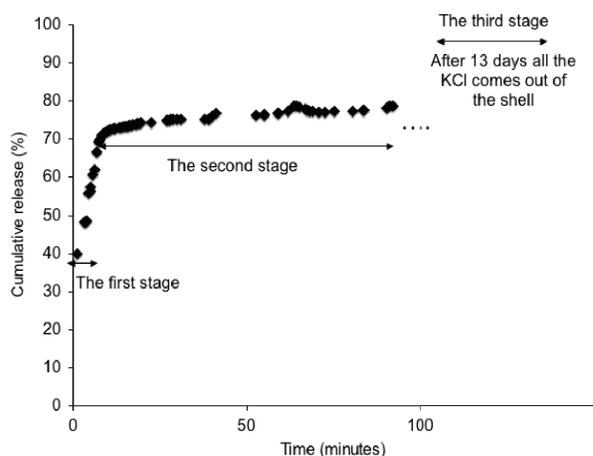


Figure 4: Release profile of KCl from hollow particles

release from 71.7% to 99% of the total amount of the salt. Beyond this point, no further increase in conductivity is observed. To confirm this result, TEM image was taken after 14 days and no KCl was observed in the hollow particles.

By comparing the uncoated KCl dissolution release in water with the coated KCl, the polymer shell around the KCl particles delayed the salt dissolution in water. This study is comparable with Shao et al. result[19]. They studied the cefradine release profile from porous hollow silica nanoparticles and showed a delayed dissolution effect. Cefradine dissolves in water from the shell within 12 hours while it takes several days for us to dissolve all of the coated KCl. But the pattern of the etching is almost the same. First they observed a fast release, then a slower stage and finally reached a constant concentration which is almost the same as our result.

## 4 CONCLUSION

In summary, we developed a method to synthesize hollow nanoparticles by a template-dissolution process. First, we deposit a plasma polymer by the plasma enhanced chemical vapor deposition technique. Then the template is dissolved to produce a hollow nanoshell. The hollow particle shell has a uniform thickness as it is shown in TEM images and is intact after mixing with HF acid. One of the interesting behavior of hollow particles is their permeability which was studied in this work by measuring the profile release of KCl from the hollow shell. The concentration of the coated KCl is detected by a conductivity meter and is measured over a long period of time. The hollow particles exhibit a delayed release response which can be used in encapsulation applications.

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