Video Article

Encapsulation and Permeability Characteristics of Plasma Polymerized Hollow Particles

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Abstract

In this protocol, core-shell nanostructures are synthesized by plasma enhanced chemical vapor deposition. We produce an amorphous barrier by plasma polymerization of isopropanol on various solid substrates, including silica and potassium chloride. This versatile technique is used to treat nanoparticles and nanopowders with sizes ranging from 37 nm to 1 micron, by depositing films whose thickness can be anywhere from 1 nm to upwards of 100 nm. Dissolution of the core allows us to study the rate of permeation through the film. In these experiments, we determine the diffusion coefficient of KCl through the barrier film by coating KCL nanocrystals and subsequently monitoring the ionic conductivity of the coated particles suspended in water. The primary interest in this process is the encapsulation and delayed release of solutes. The thickness of the shell is one of the independent variables by which we control the rate of release. It has a strong effect on the rate of release, which increases from a six-hour release (shell thickness is 20 nm) to a long-term release over 30 days (shell thickness is 95 nm). The release profile shows a characteristic behavior: a fast release (35% of the final materials) during the first five minutes after the beginning of the dissolution, and a slower release till all of the core materials come out.

Video Link

The video component of this article can be found at http://www.jove.com/video/4113/

Protocol

1. Preparation of Silica Nanoparticles for Deposition

1. Starting with dry silica powder, prepare the sample for coating by first eliminating large aggregates.
2. Wash silica particles (diameter of 200 nm, purchased from Gel-Tec Corp.) with ethanol (190 proof pure) and leave the sample under a fume hood till all the moisture evaporates with ethanol.
3. Sift particles through a series of metallic meshes (US # 100-400) in order to break any remaining agglomerations.
4. Place particles and a small magnetic stirrer bar in the tubular reactor, as shown in **Figure 1**. Particles should be placed inside the plasma zone.
5. Seal the glass reactor by placing an o-ring between two flanges, one at the end of the glass tube and one at the end of the pipe connected to the pump.
6. Install the stainless steel clamp ring around the flanges and hand tighten the screw around the clamp.

2. Preparation of the Vacuum System

1. Fill the liquid nitrogen trap, then allow the surface of the trap to become cold. Wait 5 min.
2. Add isopropanol in the bubbler and connect to the plasma reactor.
3. Seal the bubbler by placing a rubber o-ring around the metal pipe and tighten the nut till the place of pipe to bubbler connection becomes sealed.

3. Plasma Deposition Process

1. Place the bubbler in a water bath with temperature of 34±2 °C.
2. Turn on the argon gas flow controller and enter 6.00 sccm as the set point.
3. Gradually open the gate valve that connects the glass tube to the pump while the pump is working. Perform this step carefully because sudden decrease of pressure may cause the particles to be blown away by the flow. Wait till the pressure reaches 200 mTorr, then leave the gate valve fully open.

4. Place the magnetic stirrer under the glass tube and set the speed at 100 rpm.
5. Connect the aluminum ring around the tubular glass reactor to the radio frequency, RF, generator and connect the stainless steel clamp to the ground.
6. Turn on the matching network (ENI MW-5D) first and then switch the AC line and the RF generator power on. Set the power at 30 W for the entire process.
7. After a specific duration of time (10, 20, or 40 min) turn off the matching network, RF generator, and the AC power respectively.
8. Close the check valve and then turn off the argon flow controller. Disconnect the bubbler from the valve and gradually increase the reactor pressure to atmospheric.
9. Open the clamp and transfer the particles from the tube into a plastic dish using a metallic spatula.

4. Preparation of Hollow Particles by Dissolution of Core Material

1. Place the sample under a fume hood for the entire process of adding hydrofluoric acid.
2. Hydrofluoric acid is an extremely corrosive acid and exposure of eye and skin to it may cause permanent damage. Use goggles with a face shield and wear a laboratory coat when handling HF.
3. Mix 10 ml of hydrofluoric acid (Aldrich 49%) with 10 ml deionized water and add to the plastic dish that contains the coated particles.
4. Place the plastic dish on a magnetic stirrer and allow the core to dissolve for 24 hr.
5. After one day dilute the sample with 50 ml deionized water and centrifuge the sample for 1 hr. Discard the liquid layer at the top in a plastic container and transfer the bottom layer that contains the particles in a plastic Petri dish.
6. Add 50 ml deionized water and vortex the sample and centrifuge it again. Dispose of the top layer and transfer the particle layer in a clean Petri dish.
7. Wash the particles with ethanol, air dry the sample, and transfer hollow particles into a vial with cap and keep the particles in a desiccator.

5. Characterization of Permeability (Rate of Core Release)

Materials: Potassium chloride for core materials

1. Prepare 0.001 molar potassium chloride (KCl) solution by mixing 0.0745 grams KCl with 1 liter deionized water.
2. Fill the glass bottle of constant output atomizer model 3076 and install the bottle cap.
3. Connect the compressed air hose to a membrane dryer, which is connected to the gas inlet of the atomizer. Then attach a filter to the outlet hose in order to collect KCl nanoparticles.
4. Gradually open the compressed air valve and let the air flow through the membrane dryer. Allow the particles accumulate in the filter for 5 hr.
5. Close the compressed air valve and carefully remove the filter and collect the particles. Place the particles in a desiccator prior to the coating process.
6. Follow protocol 2 and 3 in order to obtain uniformly coated KCl particles.
7. Mix coated KCl with 10 ml deionized water in a glass vial. To fully mix the sample, drop a magnetic stirrer into the solution and leave it on a magnetic stirrer. Incubate the sample at 25 °C.
8. Insert the conductivity meter probe (Thermo Orion model 105) into the vial and record the conductivity over 30 days.

6. Representative Results

We have applied this process to a variety of core materials, including oxides (silica), salts (KCl) and metals (Al), as shown in **Figure 2**. Transmission electron microscope has been used to confirm the radial uniformity of the films and to measure their thickness. We have successfully coated particles ranging from 37 nm to 200 nm in diameter (**Figure 2**) but there is no fundamental limitation on the size of particles that can be treated by this method. The rate of shell deposition is approximately 1 nm/min. This rather slow rate makes it possible to control the thickness of the films quite accurately via the deposition time. The plasma-polymerized shell is a permeable barrier, as demonstrated by the fact that the core material can removed by etching or dissolution. **Figure 3** shows the hollow shells that remain after the silica core is removed. The removal of the core is complete and the radial uniformity and thickness of the films are quite high. For the purposes of evaluating the permeability through these films, we switched to KCl as the core material since the dissolution of KCl can be monitored very easily through the ionic conductivity of the solution. **Figure 4** shows the release of KCl from the core for four samples with different thickness, 20 nm, 40 nm, 75 nm, and 95 nm, respectively. Coated KCl particles were suspended in water and the conductivity of the solution was followed for a period of 30 days. In addition to the four samples, a control that consists of uncoated KCl particles was also monitored. Uncoated KCl particles dissolve within a very short time of approximately 1 min. By contrast, coated KCl shows a significantly slower release rate. The release profile of the coated particles is characterized by initial burst that takes place within the first hr, followed by a much slower release that takes several days to complete, depending on the thickness of the film.
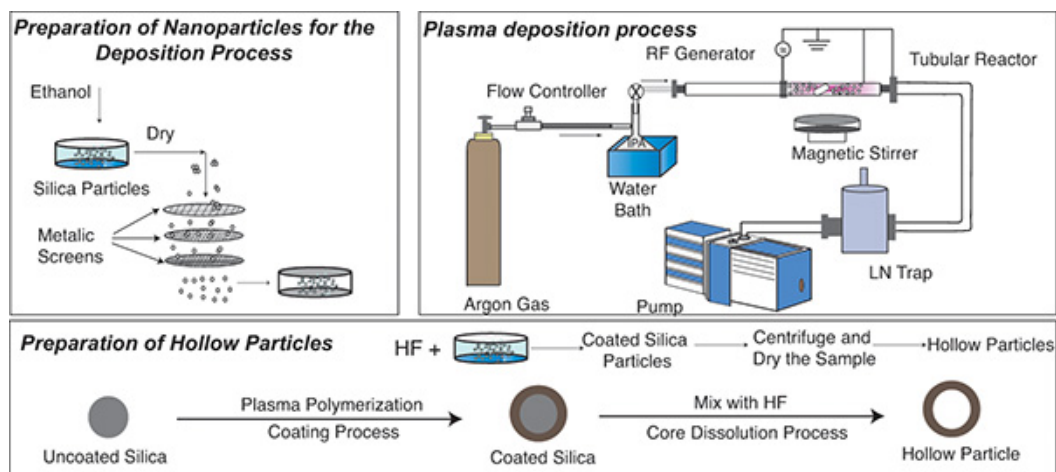
Figure 1. Schematic representation of the preparation of nanoparticles, plasma deposition, and hollow particle formation.
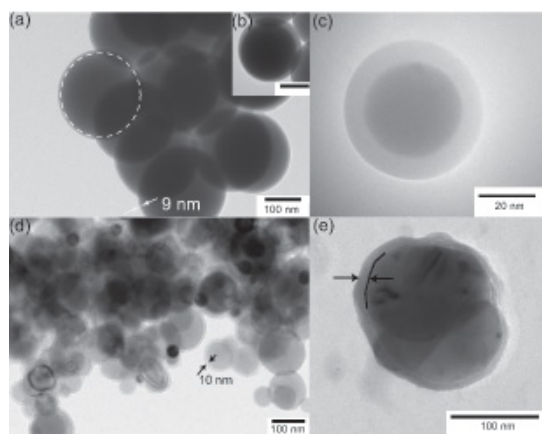

Figure 2. TEM images of coated (a), (b) silica particles with d=200 nm, (c) silica particle with d=37 nm, (d) aluminum with d~100 nm, and (e) KCl particle with d=100 nm
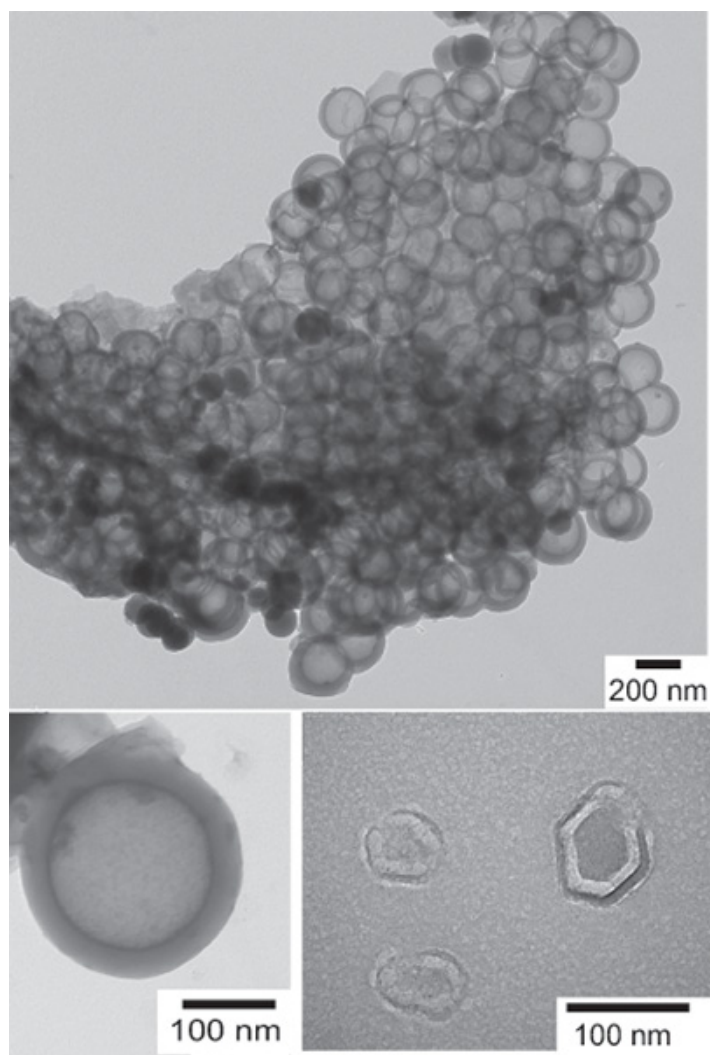
Figure 3. TEM images of hollow particles after etching the (a), (b) silica core with diameter of 200 nm, and (c) KCl core.
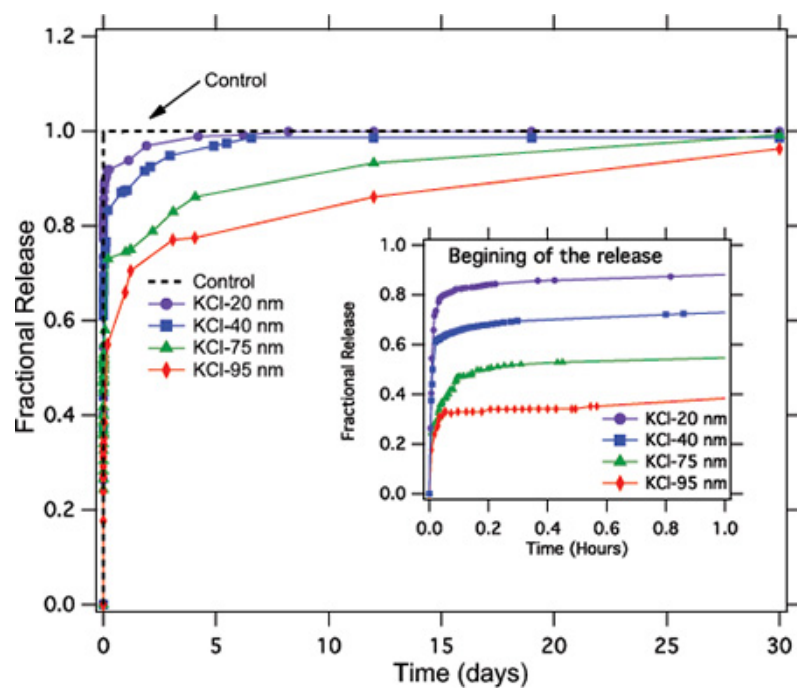
Figure 4. Effect of shell thickness on the release profile. The inset graph shows the release during the first hr.

Discussion

One of the biggest challenges in coating nanoparticles is to provide a compatible chemistry between coating and the substrate [1,2]. The methodology described here has the advantage that it is not material-specific. Plasma polymers show excellent adhesion on a variety of substrates, including hard metals (**Figure 2(c)**), silica (**Figure 2(c)**), silicon, or soft materials (e.g., polymers) without the need for any special surface modification [3,4,5]. The technique has the further advantage that it is not limited by the size of the core particle and is easily adaptable to particles in the nano- and micrometer range. The thickness of the coating is controlled by the deposition time and can be easily varied from few to several hundred nm. Another level of control is provided by the organic precursor that is used to produce the coating. For example, the hydrophobic character of the coating can be varied by suitable selection of the precursor [6]. One aspect of the process in need of further improvement is achieving the uniformity of coating. We estimate that approximately 70% of the particles treated in the plasma become fully coated with the remaining 30% showing partial coating. Designing and engineering a new reactor in which plasma surrounds all around the particles during the entire process can improve this.

Disclosures

No conflicts of interest declared.

Acknowledgements

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