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Control of particle and pore size in nanoporous Pd powders

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Abstract

Palladium (Pd) is commonly used as a storage and separation material for hydrogen. Nanoporous forms of Pd allow for increased transport rates of hydrogen between the gas and metal hydride phases due to greater surface area, and are expected to have greater cycle life because the pores help accommodate the volume change during charging and discharging. Not only is pore size important in these storage materials, but particle size also plays a key role in controlling fluid flow through a packed powder, or particle transport in a flow battery. We use less noble metal particles of well-defined size as reducing agents that are geometrically self-limiting, so the resulting Pd particles should not exceed this size. By this approach, we can control both the particle and pore size of nanoporous Pd powders, which should allow optimization of hydrogen charging and discharging rates in macroscopic samples. Compared to previously reported strategies to control particle size, ours is a more scalable and inexpensive technique to produce nanoporous metals.

Introduction

Hydrogen fuel cell technology is among the most promising alternative energy systems being developed to replace fossil fuels. Metal hydride batteries are frequently used in electric vehicles due to their safety and reliability.[Burke, 2007] The power densities of both of these technologies are limited by rates of chemical reactions at electrode surfaces, and their lifetimes are often limited by changes in electrode geometry.[Long, 2004] This often leads engineers to use oversized batteries or fuel cells to compensate for these limitations. Efficiency and range are impacted if a battery cannot absorb braking energy rapidly enough in an electric vehicle.[Robinson, 2009] Nanoporous Pd can provide faster charging and discharging in hydrogen gas storage systems, and accommodate swelling and shrinking of electrodes.[Cappillino 2013] While Pd is too expensive for many applications, study of this material may lead to increased efficiency, reliability, and range of the more general class of hydrogen powered batteries and systems. Developing an easy and inexpensive method to produce nanoporous Pd would ease further research and development of clean energy technology to help reduce our overall dependency on fossil fuel.

Pd in particular has a number of advantageous properties that make it a prime choice for these systems. Pd has the ability to absorb up to 900 percent of its volume of hydrogen at room temperature and pressure, and then release it with only mild heating or pressure reduction.[Lewis, 1960; Flanagan, 1991] The rate of uptake and release can be fast, but often limited by such factors as surface area, particle size, and packing density. We seek to optimize these properties in order to improve upon current energy storage and conversion technologies that rely on the chemistry of hydrogen.

Nanoporous noble metals with highly uniform, ordered pores are usually made by reduction of metal salts in the presence of a surfactant.[Attard, 1997] The surfactant is at high enough concentrations that it forms arrays of cylindrical (or more complex) micelles a few nanometers in diameter, around which the metal is grown. The surfactant is then washed away. The metal can be reduced by electrodeposition on an electrode,[Bartlett, 2002] use of a solution-phase reducing agent like ascorbic acid,[Robinson *et al.*, 2009] a gas-phase reducing agent like hydrogen,[Robinson, 2010] or a solid-phase reductant like zinc metal.[Sugimoto, 2012] The surfactant usually contains a poly(ethylene oxide) hydrophilic end. The hydrophobic end can be a long-chain alkyl group such as hexadecyl, or a hydrophobic polymer such as polystyrene.[Cappillino, 2013] Adjusting the surfactant size allows tuning of the resulting pore size.

While these methods can reliably produce highly regular pores, there is much less control over larger-scale geometry. An example from previous work in our laboratory is shown in Figure 1. In this case, uniform, regularly spaced pores are apparent at the scale of hundreds of nm, but the material arranges into irregularly shaped flakes on the 10 um scale. Particle size is a complicated function of the transport rates of the metal salt, reducing agent, and growing particles through the surfactant mixture, and typically has highly heterogeneous results. Planar processing methods have been reported that control both particle and pore size, but they require many steps and generate only about a milligram per batch.[Chae, 2012; Ji, 2003] We have developed a scalable strategy to control both the particle size and pore size in nanoporous Pd powders. We first create uniform-sized, nonporous particles of copper, a metal that is less noble than Pd. We then use these as self-limiting reducing agents for a palladium salt. , The Pd should react 1:1 with the copper, resulting in a similarly sized porous Pd particle and a copper salt. This galvanic exchange reaction has been previously used in the production of nanoparticles and nanowires [Badri, 2000; Lu, 2010] and in growth of multilayer films.[Sheridan, 2013] In practice, some of the copper remains in the form of an alloy [Lu, 2010] that still retains useful hydrogen storage properties. By this approach, we can produce micrometer-scale Pd alloy particles of uniform shape and size that can be consistently reproduced. Our work contrasts with the prior work on nanowires and films because it involves larger scale particles in larger scale batches, while maintaining control over pore size. We expect to be able to adjust the particle and pore size by changing the surfactant or the reductant particle size. By adopting a literature procedure that uses inexpensive, dilute surfactants,[Wang, 2012] we are able to routinely synthesize batch sizes large enough for many important characterization methods, enabling further research and development of these materials.

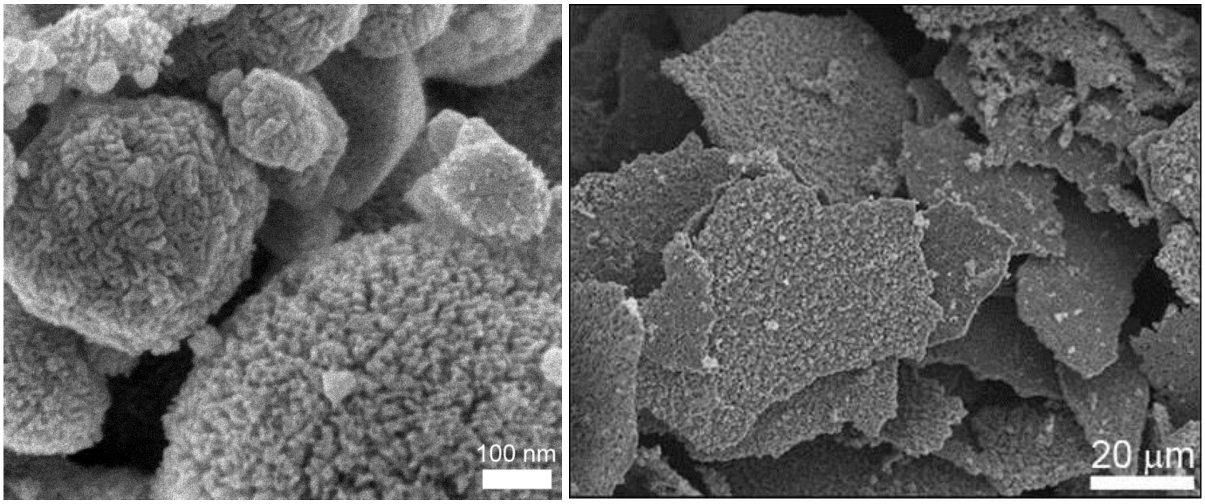


Figure 1: Nanoporous Pd reduced by H_2 gas in a block copolymer template, produced according to [Cappillino, 2013] shows highly ordered pores (left) but uncontrolled particle shape and size (right).

Experimental

Materials

Copper sulfate was obtained from EM Science. Sodium ascorbate was obtained from Aldrich. sodium chloride, acetone, ammonium tetrachloropalladate and palladium nitrate. Pluronic F127 is a low-cost triblock copolymer from BASF with hydrophobic poly(propylene oxide) in the middle, with a degree of polymerization of about 56, and hydrophilic poly(ethylene oxide) on the ends, and each end with a degree of polymerization of about 101, containing about 0.01% BHT as an antioxidant.

Synthesis of Cu particles

A solution of 6 mL 1 M copper sulfate was added to a 10 mL solution of 2 M sodium ascorbate at room temperature. After approximately 2 minutes, the solution begins to change from a dark brown to an orange/yellow color. Within 2 – 4 minutes when a yellow color has fully developed throughout the solution, 1 mL 10 wt % Pluronic F127 is added to the reaction. The addition of a surfactant does not result in pores in the copper, but helps to reduce settling or aggregation of the particles. This process does not require any stirring or excess agitation which can cause uneven particle formation.

To ensure adequate reaction time, the solution was left for 24 hours. After 24 hours a noticeable copper precipitate had formed on the bottom of the vial. The copper and remaining solution were placed in a centrifuge tube for washing and extraction. The copper was first centrifuged at 8000 RPM for two minutes. The supernatant was then removed and the copper was re-suspended in 1.0 wt % aqueous Pluronic F127, and again placed in the centrifuge for 2 minutes at 8000 RPM. This process was repeated 3 times in order to thoroughly remove any remaining reactants from the suspended copper solution. After the third wash, the copper was again suspended in 100 mL 1.0 wt % F127 for use as a reducing agent. The particles were used in subsequent steps immediately, or within a few days, being stored in a sealed container. Before storing, nitrogen was bubbled through the solution of suspended particles to slow the rate of oxidation.

Synthesis of Pd particles

To prepare the palladium reactant solution, 1.0 wt% Pluronic F127 surfactant is dissolved in an aqueous sodium chloride solution (135 mL, 3.5M). After the surfactant has been fully dissolved, $(NH_4)_2PdCl_4$ (1.34 g, 4.71 mmol) is added to the solution and lightly stirred until fully dissolved. The 100 mL of suspended Cu particles prepared above (containing 299 g, 4.71 mmol Cu) was slowly added to the Pd solution with continuous stirring. This resulted in a gradual change of color from light brown to black over the course of approximately 10 minutes. Prior to this mixing step, nitrogen was bubbled through the suspension of Cu particles and the Pd salt solution to remove oxygen and reduce the rate of oxidation over the reaction period. The mixture was then left stirring while nitrogen was once again bubbled through. After another 10 minutes, the nitrogen line was removed and the flask was capped immediately. The reaction then remained stirring for 48 hours. After 48 hours, the formation of a black precipitate was noticeable on the bottom of the flask. The solution was placed in the centrifuge at 4000 RPM for 3 minutes. The remaining supernatant was discarded and the powder was re-suspended in 30 mL of acetone and again centrifuged at 4000 RPM for 3 minutes to remove impurities. The acetone wash cycle was repeated 3 times followed by a DI water wash cycle using the same procedure. After both wash cycles were complete, the powder was placed under vacuum and left to dry overnight.

Treatment to reduce copper content

Samples of nanoporous Pd (50 mg, X mmol) were added to two solutions of $Pd(NO_3)_2$ (10 mL, 11.8 uM, and 10 mL, 23.6 uM) and allowed to react for 24 hours to remove residual copper. These treatments corresponded to a 2:1 and 2:3 molar ratio of $Pd(NO_3)_2$ to Cu, respectively based on estimations of compositional analysis using EDS data. The suspension was then centrifuged at 4000 RPM and the treated powder was collected. The powder was washed three times by suspending in 30 mL DI water and centrifuging and then dried overnight under vacuum.

Characterization

Scanning Electron Microscopy (SEM) was used to analyze the copper and palladium powders. SEM analysis was performed using both a JEOL JSM 7600F field-emission electron microscope and a Hitachi S-4500 field-emission electron microscope. Powder samples were spread over carbon tape placed on a silicon wafer for analysis. Energy-Dispersive X-ray spectroscopy (EDS) was also performed using the JEOL JSM 7600F field-emission electron microscope.

Porosimetry analysis was conducted using a Micromeritics ASAP 2020 porosimeter. Using nitrogen at 77 K as an adsorbate gas, BET surface area [Lowell, 2004] and BJH pore size distribution [Barrett, 1951] were obtained for Pd particle samples. Pd samples were degassed for 15 hours at 50°C before performing the analysis. Hydrogen storage properties of Pd samples were also measured using this instrument. Prior to measurements, Pd samples were cleaned to remove surface oxide by exposing samples to 8 Torr hydrogen gas at 298 K, then evacuating [Cappillino, 2013]. This cleaning process was repeated three times.

Results and discussion

Our overall strategy is to use a locally constrained dose of reducing agent to produce particles of controlled size. Metals less noble than palladium provide a potentially low cost reducing agent. The metals have a molar volume comparable to our desired product, so we expect to be able to straightforwardly tune the product particle size by choosing a similar reductant particle size. There are numerous published procedures for chemical [Muzikář, 2006] and thermal [Cong, 2009] production of uniform micrometer-scale particles. We modified a literature procedure [Bicer, 2010] to create micrometer-scale copper particles by a simple, minimally hazardous reaction. Nickel, iron and cobalt are other convenient candidate materials, but they can aggregate due to magnetic interactions, and nickel and cobalt are more hazardous. Each case requires optimization to ensure that the reaction goes to completion, and that side reactions and byproduct formation are controlled.

Synthesis of uniform Cu particles

The use of copper particles with tunable morphology as a reducing agent provides great flexibility. Parameter variation during Cu synthesis such as reaction temperature, concentration and addition of surfactant has been shown to affect Cu particle shape and size. This provides the ability to tune Cu particle shape and size to desired specification. In this case, uniform spherical Cu particles (figure 2) were chosen to produce Pd spheres with a narrow size distribution that replicates the copper particles. This spherical shape maximizes surface area and is expected to exhibit ideal flow kinetics characteristics in anticipated hydrogen storage applications.

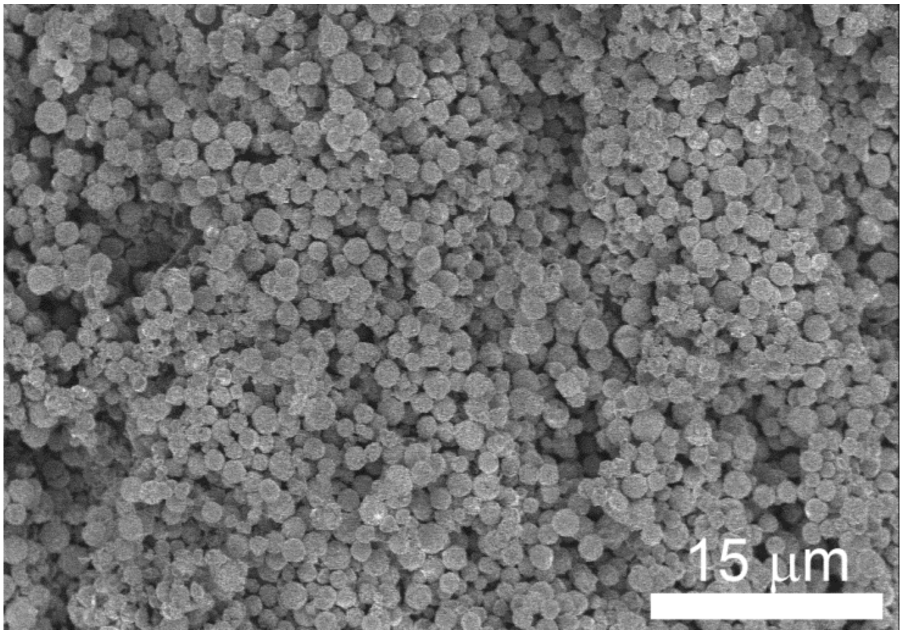


Figure 2: SEM image of uniform copper particles with a narrow size distribution

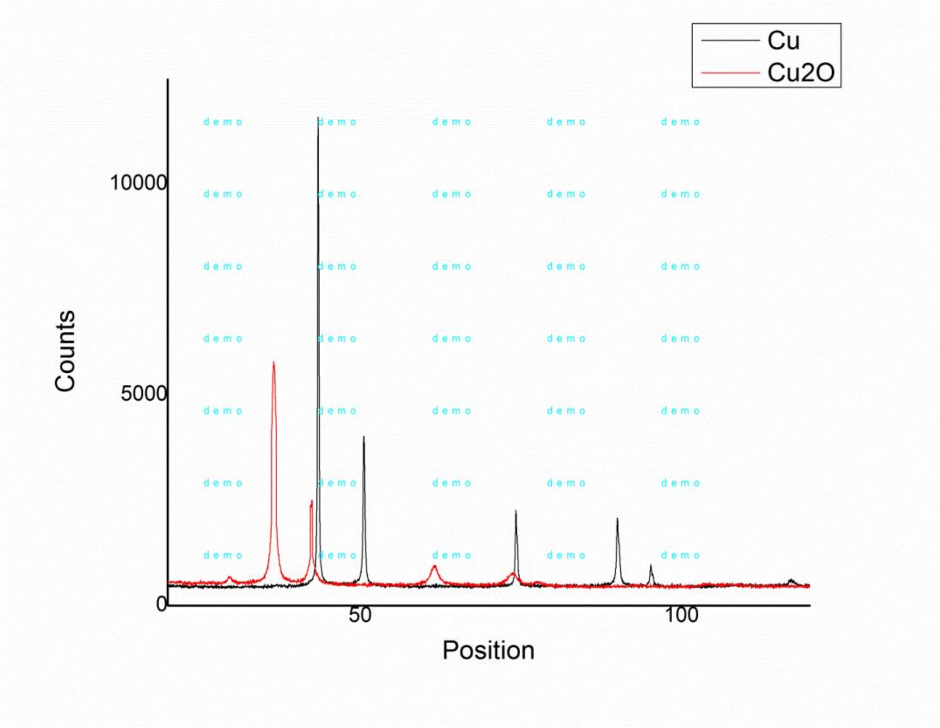


Figure 3: XRD analysis confirms a two stage reaction where Cu_2O is produced as an intermediary product and pure Cu is the final product

The copper reduction reaction appears to occur in two stages. After the solutions are first mixed there is an initial color change to a tan-colored, insoluble product. The reaction then proceeds to form a dark red-brown product, which is most likely to be copper metal. A sample of both the intermediary product and final product were analyzed using X-ray diffraction (XRD) to determine their composition (figure 3). Results indicate that the initial reaction produces Cu_2O as an intermediary where as the final product is pure Cu as expected.

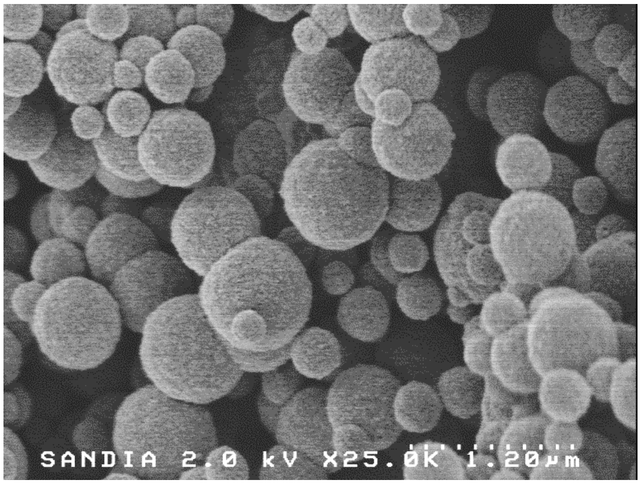


Figure 4: Intermediate Cu_2O particles produced mid reaction are smaller and have a much greater size distribution than fully reduced Cu particles

An SEM anaylsis of the Cu_2O intermediary reveals that although particle shape remains similar, overall particle size is significantly smaller and appears to have a much wider distribution. Based on SEM imaging, particle sizes were shown ranging from 300 nm to 1 µm. Initial experiments were conducted on the Cu_2O particles to determine their effectiveness as a possible reducing agent for Pd particle synthesis. A similar chemical reduction process to that used for Cu metal particles was conducted on samples of Cu_2O particles. However, significant control over particle shape and uniformity could not be achieved. Although little success was achieved through using Cu_2O, these particles may still be useful in the future with further investigation of the reduction chemistry.

This strategy is not expected to succeed unless the copper particles are isolated in solution, and not aggregated. Initial Cu reactions without the inclusion of surfactant appear uniform in SEM imaging, but in the subsequent reactions yielded large aggregates and less uniform palladium particles. In an attempt to prevent aggregation, a small amount of surfactant was added shortly after mixing the $CuSO_4$ and sodium ascorbate, in an attempt to solubilize the intermediate, but not interfere with its formation. By varying the timing of the addition of surfactant in the Cu reduction reaction, differences in the amount of aggregation were observed. Figure 5 shows three samples of Cu particles in which the surfactant has been added at various timepoints during the course of the reduction and one sample without the addition of surfactant. Adding surfactant too early to the reaction reduced uniformity by hindering the assembly of sub-micrometerparticles into micrometer-scale spheres (figure 4a). The growth mechanism of the Cu(I) intermediate thus appears to be different from what we will describe, and what has been observed previously for growth of metals.[Wang, 2012] We did not observe porosity in the Cu particles regardless of when surfactant was added. The surfactant apparently interacts with the Cu(I) intermediate differently from its interaction with the metals in the subsequent reaction. Best results were observed when surfactant was added approximately 3 – 4 minutes after the initial reaction, although the effect of addition later in this reaction was not very significant. Although spherical particles have been formed without the use of a surfactant, this often causes aggregation during subsequent steps, which results in poor uniformity in the Pd reaction. This time window for surfactant addition allows ample time for particles to form during the initial reaction period while still remaining adequately suspended as necessary for Pd reduction.

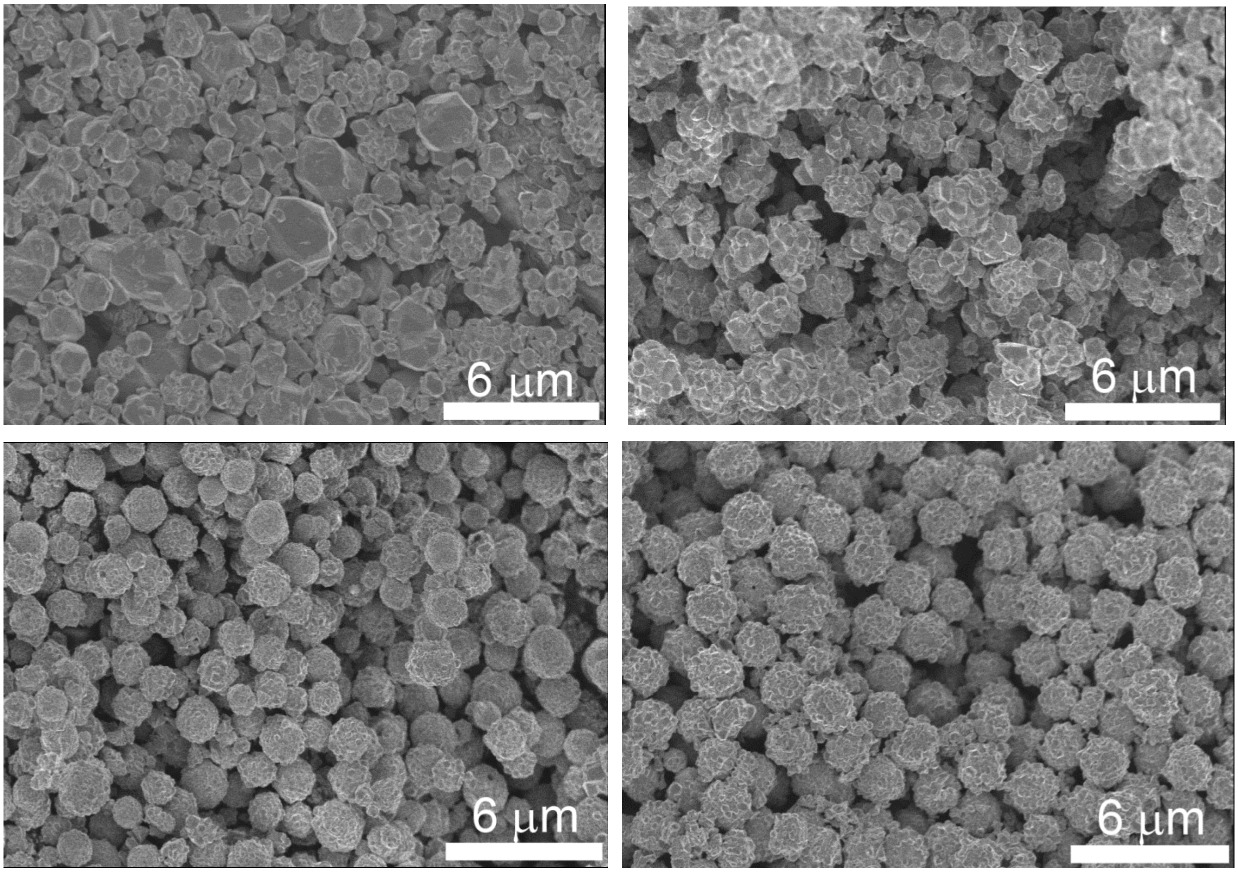


Figure 5: Cu particles with surfactant added at 1 minute (a), at 2 minute (b), 3 minutes (c), and without (d).

Synthesis of porous Pd particles

To make porous Pd particles of the same size and shape as the initial Cu particles, we react the copper with an aqueous Pd salt in the presence of a surfactant that leads to pore formation. Efforts are required to control the rate and extent of the reaction, and control byproduct formation.

Much of the prior work on synthesis of porous metals uses concentrated aqueous surfactants, but Wang *et al.* demonstrated that dilute surfactants can form pores when growth occurs at a predefined metal interface at a controlled rate.[Wang, 2012] The high viscosity of concentrated surfactants makes them inconvenient to prepare, sensitive to temperature, prone to entrainment of gas bubbles, and slow as a reaction medium due to the inhibition of convective mass transport.[Robinson, 2009] The ability to use dilute surfactants thus conveys a significant advantage.

Here, we use one of the surfactants studied by Wang *et al.*, Pluronic F127, a low-cost triblock copolymer from BASF with hydrophobic poly(propylene oxide) in the middle and hydrophilic poly(ethylene oxide) on the ends.[Wang, 2012] This group reported that this and other surfactants yield pores when electroplating a platinum film using 1.0 wt % surfactant solutions. Surfactant concentrations closer to 50 wt % are typically used when making nanoporous metals. When dissolved, the F127 surfactant forms spherical micelles within the solution, according to the phase diagram in [Wanka, 1994]. At electrode or particle surfaces, the effective concentration is probably higher due to adsorption of a surfactant layer onto the surface, and this may allow for formation of a 2D hexagonal or disordered close-packed structure on the surface. Pluronic F127 was shown to yield pores around 12 nm in diameter.[Wang, 2012]

Upon mixing, the Cu particles begin to reduce the Pd ions. As Pd ions are reduced, Pd metal forms within the surfactant template. Reduction reactions are carried out in the presence of a high concentration of NaCl to slow the reaction and prevent overgrowth or displacing the surfactant, resulting in reduced porosity and uniformity (Figure 6). Because Pd ions bind chloride more strongly than Cu ions, the presence of excess chloride to the reaction solution is expected to lower the reduction potential of Pd by Le Chatelier's principle (stabilizing the oxidized form) more than that of Cu, reducing the reaction overpotential and slowing the chemical reduction process.[Sheridan, 2013] This deceleration provides more controlled growth rate during the reaction, resulting in a more uniform particle distribution.

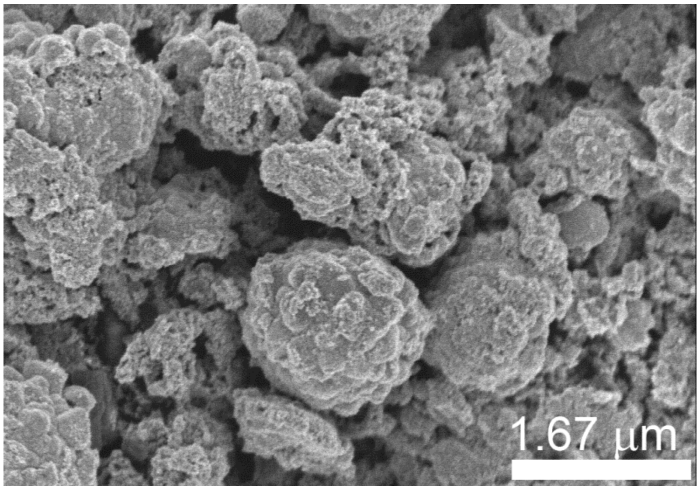
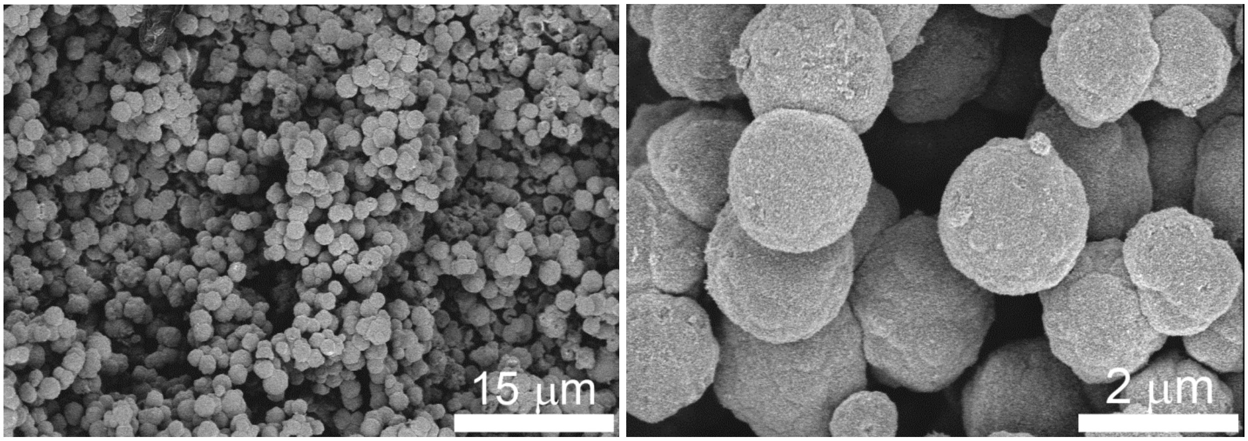


Figure 6: Pd-Cu reactions without chloride results in uncontrolled particle growth

Utilizing a slow and controlled growth rate, Pd metal forms within the surfactant template as it is reduced. After the Pd metal has been fully reduced, a washing process is necessary to remove the surfactant template from the synthesized particles. The particles were suspended in acetone, a solvent that readily dissolves the surfactant, and centrifuged in order to remove residual surfactant. Using a centrifuge speed of 4000 RPM has proven to be ideal due to the particles' tendency to crumble at higher RPMs. After a thorough wash process, the surfactant is removed, revealing a uniform-sized pore structure in its place.



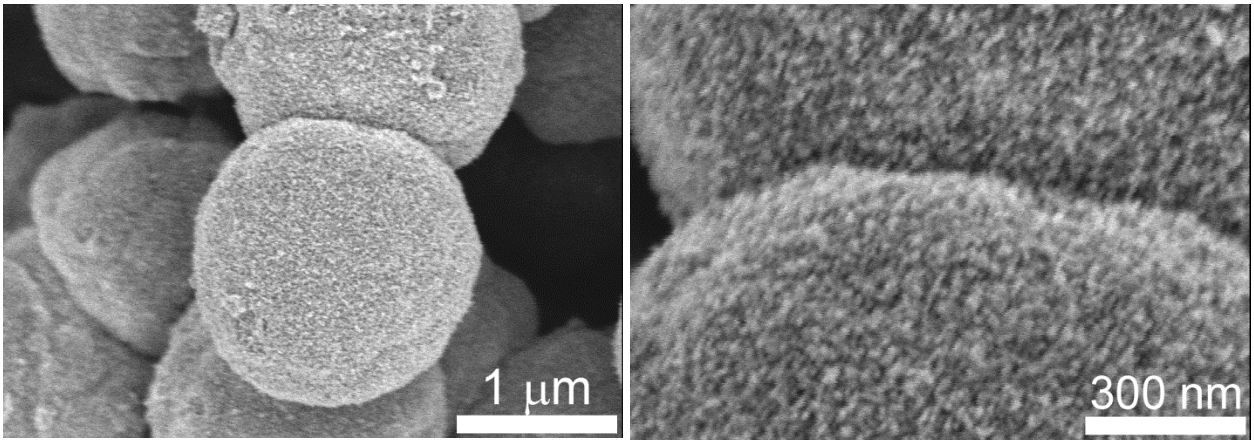
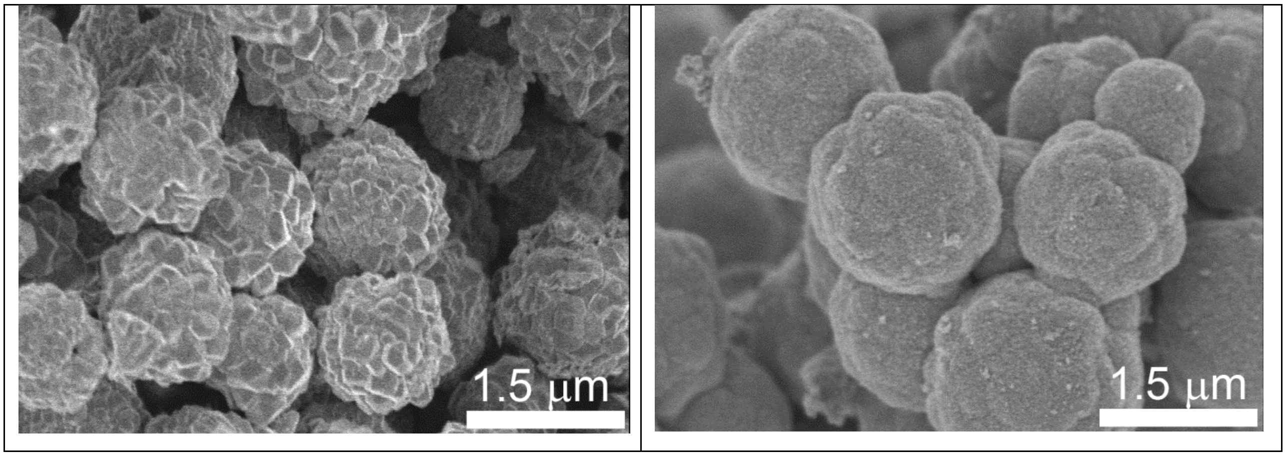


Figure 7: SEM images of Pd sample at x2.00k (a), x15.0k (b), x30.0k (c), x100k (d)

Physical characterization of the Pd particle morphology was conducted with SEM imaging after the chemical reduction process. Particle shape and size is observed to be fairly consistent, with spherical particles of similar size throughout the sample. As shown in Figure 7, Pd particles with size and shape similar to the Cu particles used as reducing agents range from 1-2 µm in diameter. SEM images at higher magnification also revealed a highly porous surface (Figure 7d). Pore sizes range from approximately 10 – 20 nm in diameter on the particle surface. This surface porosity appeared uniform among particles.

The use of well suspended and uniform copper particles is critical to producing uniform size palladium particles (Figure 8a-b). Earlier attempts at creating uniform spherical palladium particles using less uniform or aggregated copper produced similarly aggregated palladium with a relatively broad size and shape distribution (Figure 8c-d). The described Cu preparation procedure instead reliably provides uniform Cu particles.



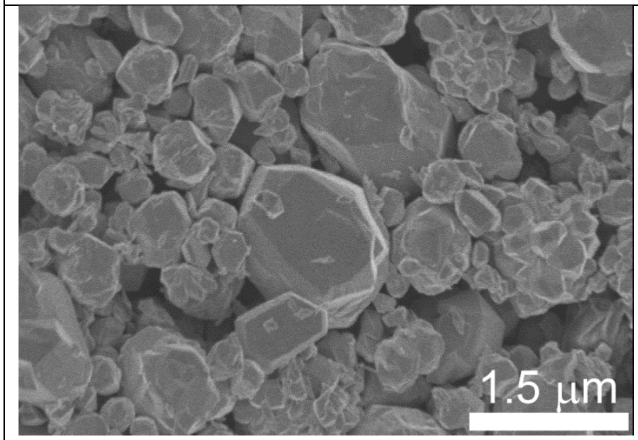
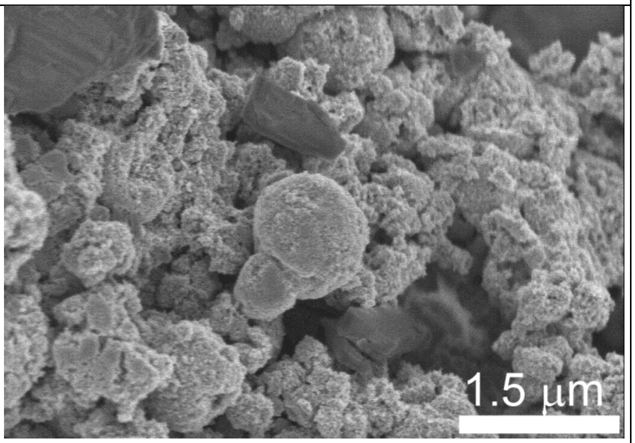
Cu	Pd
	

Figure 8: Uniform Cu particles (a) produced similarly uniform Pd particles (b), whereas non-uniform Cu particles (c) produced Pd with less uniformity (d).

Variation of other synthesis parameters from the prescribed procedure often produced less desirable results. Preparations using very low and very high chloride concentrations in the initial reaction solution showed a reduction in overall uniformity of the Pd particles. Additionally, length of reaction time was observed to be an important factor in producing uniform Pd particles. For reactions lasting longer than 48 hours, there was noticable degredation of particle uniformity. Reaction time also had an effect on the degree to which the copper metal within the reductant particles was oxidized by oxygen. For reactions exposed to oxygen, a green insoluble precipate was observed after 24 hours. This is remedied by bubbling nitrogen through the reaction solution to remove oxygen present in the flask. Although nitrogen limits the amount of oxidation durring the reaction, it has no effect on particle degredation due to increased reaction time.

The described procedure has been scaled up to 50x the initial size of preliminary expereiments with negligible change in results. Because the reactions are dilute, slow, and not extremely exothermic, scaling up is relatively straightforward and requires little modification from the standard procedure. It is expected that further scaling could be easily achieved using larger quantities of reagents.

Elemental composition

Compositional characterization was conducted using EDS, in order to determine whether residual copper was present within the Pd particles. Unreacted copper is inert with respect to hydrogen, so it is essentially a diluent in a hydrogen storage material. Residual copper in the form of a palladium alloy can influence the hydrogen storage properties of the product, as previous studies have shown.[R. Burch and R.G. Buss, "Absorption of Hydrogen by Palladium-Copper Alloys." J. Chem. Soc. Faraday Trans. 1 vol. 71 p. 913-921 (1975)] Residual copper salts such as copper oxide or copper hydroxide are undesirable because they tend to be insoluble, and thus difficult to wash away, and could foreseeably react with hydrogen to form water. Table 1 indicates that particles are composed of ~60% Pd and ~40% Cu, so clearly a significant amount of copper still remains within the particles. In this range of copper content, hydrogen storage properties are significantly diminished [Burch, 1975], thus a method to partially remove the copper was developed as described below.

To quantify surface area and measure pore size distribution (PSD), nitrogen porosimetry was performed (Figure 9). Porosimetry was also conducted on a powder sample of porous Pd after fully hydriding and dehydriding. This demonstrated that the PSD is drastically affected by cycling from the metallic, to the hydrided, and back to the metallic phase.. Before cycling, a broad pore distribution can be seen from 1 – 10 nm with a total surface area of 35 m^2/g. After treatment however, average pore diameter increased showing a sharp maximum at approximately 10 nm. Furthermore, total surface area is reduced to 22 m^2/g as the pore diameter increases.

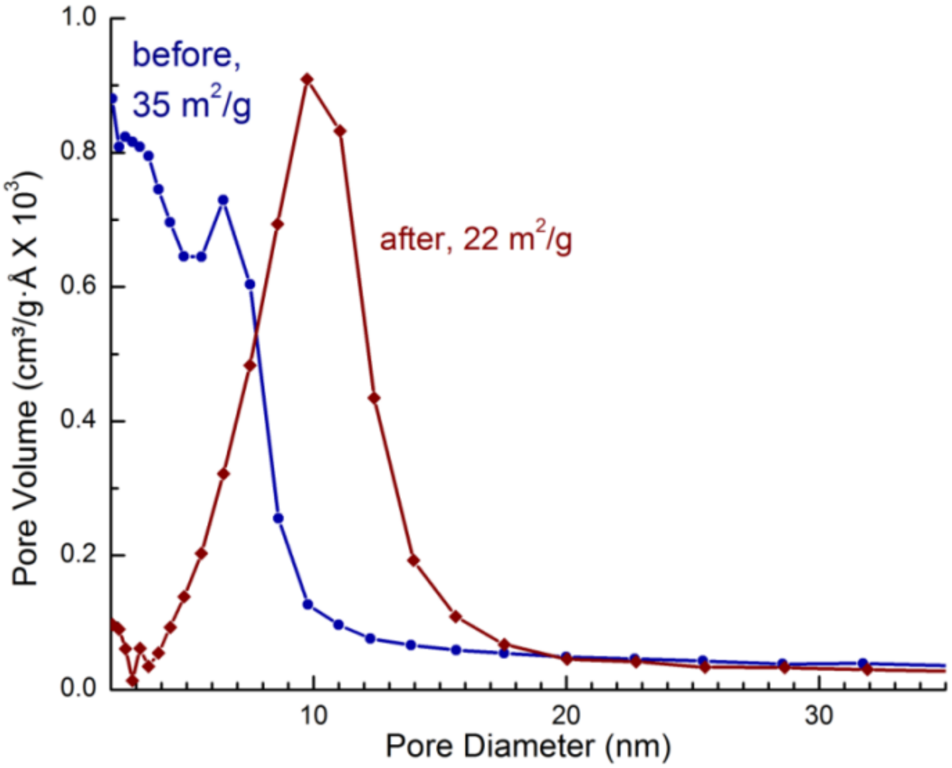


Figure 9. Pore size distribution of reaction product before and after a hydride cycle.

Apparent changes in the pore structure during hydride and dehydriding cycles may be attributed to the effects of hydrogen when absorbed within the crystal lattice of the metal. Hydrogen atoms stored within the lattice may cause the shifting and rearrangement of Pd and Cu atoms, resulting in plastic deformation of the particle structure.[Ong, 2012] The change in pore geometry caused by hydrogen cycling collapses smaller pores, causing them to coalesce into large pores, shifting the average pore diameter higher.

Hydrogen Storage

The room-temperature pressure-composition isotherms of the reaction product were measured to determine hydrogen storage capacity, and the pressure range at which hydrogen is absorbed. The samples store an appreciable amount of hydrogen, but do not reach H-to-metal ratios exceeding 0.6 in this pressure range, as is typical for pure Pd. Rather than reaching a plateau at 10 Torr of H_2 as for pure Pd, the pressure continues to increase until 100 Torr where only a slight decrease in slope is visible. The lack of a flat plateau region is likely due to a nonuniform copper distribution within the metal. To detect the presence of Cu metal, XRD analysis was performed on a bulk sample of synthesized Pd powder. XRD analysis (Figure 11) confirms the existence of both Pd and Cu metal within the powder. The existence of residual copper within the particles is likely the result of imcomplete oxidation of the copper metal during the chemical reduction process, thus resulting in a Pd-Cu alloy. Since copper atoms are most likely non-uniformly dispersed throughout the particles, hydrogen diffusion charateristics are altered causing limited absorption during hydriding cycles.

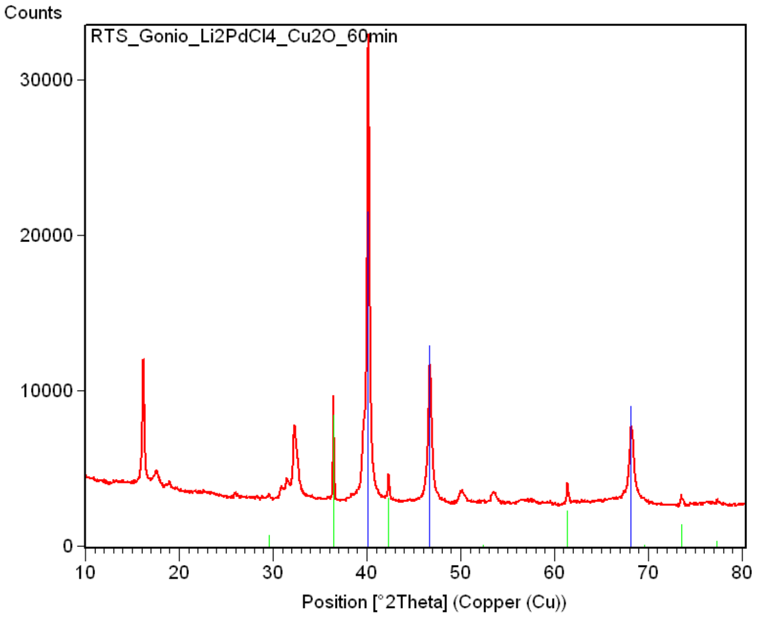


Figure 11: XRD analysis confirms particles are composed of both Pd and Cu metal

In an effort to reduce the presence of residual copper within the particles, a chemical treatment with $Pd(NO_3)_2$ was performed on the Pd powder in order to improve hydrogen storage properties. This form of palladium has a higher reduction potential than the Pd ion in the presence of excess chloride, and can be expected to be more likely to react with residual Cu in the product that is stabilized by alloying with Pd.[Bard, 1985] Given that the average EDS measurements showing the Pd particles contain approximately 40% Cu, a 50 mg sample of bulk Pd powder should contain roughly 20 mg of residual copper. We then exposed the product to a prescribed molar ratio of Pd nitrate to copper.

Element	Untreated	$1Pd(NO_3)_2$: 2 Cu	$3Pd(NO_3)_2$: 2 Cu
Cu	38.31%	25.66%	19.34%
Pd	61.69%	74.34%	80.66%

Table 1. Quantitative EDS analysis of reaction product by atomic %.

EDS anaylisis reavels samples treated with 1:2 and 3:2 ratios of $Pd(NO_3)_2$:Cu show a decrease in Cu composition. The 1:2 treatment saw a reduction to approximately 25% Cu, whereas the 2:3 treatment saw Cu composition decrease to 19.43% (Table 1). Hydrogen absorption isotherms were recorded for each of the treated samples to determine if the decrease in Cu composition made any improvement to the hydrogen storage properties of the powder. The resulting isotherms of treated samples are shown in comparison to the “untreated” sample in Figure 12. The results shown are for the second isotherm measured on the sample; the curve was higher in the first measurement, but relatively stable after that. This variation between the first and second measurements may be due to an initial redistribution (most likely a segregation) of copper during the initial hydriding cycle.

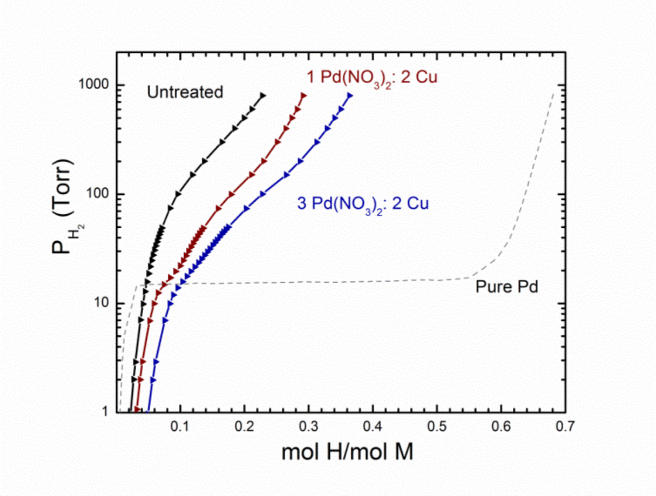


Figure 12: Pd-Cu hydrogen absorption isotherms for untreated sample, 1:2 treated sample and 3:2 treated sample. Repeated measurements showed that the first isotherm was different (higher) than subsequent measurements, so the second measurement is shown here.

In pure Pd samples, a pressure plateau at approximately 10 Torr is visible. Although a clear plateau is not visible in the treated samples, there is a noticeable decrease in slope at the 10 Torr mark, suggesting a higher Pd composition. The residual copper remaining in the treated metal is unlikely to be uniformly distributed and thus still limits the absorption and prevents a plateau which would be expected in a pure Pd sample. Even though copper is still present within the powder, the treatment process produces a noticeable increases in the hydrogen absorption capacity at both high and low pressures.

Conclusion

Through the self-limiting reaction between Pd salts and metallic copper particles in the presence of a surfactant, we have developed a straightforward, inexpensive procedure to produce uniform nanoporous Pd particles. This prodedure should produce size- and shape-tunable particles based on the physical characteristics of the copper used as a reducing agent. This approach cannot be expected to succeed if the copper particles or growing intermediates aggregate, or if many small Pd particles grow and break off of the Cu.We were able to identify reaction conditions that avoid such dead ends, yielding consistently reproducible results.

Our experience suggests that these results are scalable to even greater quantities. Even though further analysis of large scale reactions may be necessary to optimize the reduction processes, this method offers a practical approach to a palladium alloy with uniform pore and particle size. Despite the fact that residual Cu within the powder may reduce the overall absorption capabilities, a Pd-Cu alloy may be beneficial in specific applications. Pd-Cu alloys have application in such areas such as hydrogen gas and isotope separation.. Potential applications in other fields, such as medical devices or chemical separations, may also be possible in the future. [Gittard, 2010]

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