Supplementary Information

Rapid Fabrication of Core-Shell Silica Particles Using a *Multilayer-By-Multilayer* Approach

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1. Preparation of Silica Core-Shell Particles.

Silica cores (1 g) were suspended in 50 ml H_2O and the pH was adjusted to 2.7 by adding 1.0 M HNO_3. Ionic strength was adjusted to 0 - 0.5 M by adding 5.0 M NH_4NO_3. To the suspension of silica cores was added 5 ml of a 5 % (w/w) aqueous solution of positively charged PDADMA polyelectrolyte, and pH was again adjusted to 2.7 if necessary. We found that a primer layer of the widely used PE3 (PDADMA/poly(styrebesulfonate, sodium salt)/PDADMA) coating was not necessary in our work. In the silica nanoparticle coating step, to 45 mL of the PDADMA coated particles (pH = 2.7) was added 5 ml of a suspension of ~ 8 % (w/w) silica nanoparticles (pH = 2.7). Before each coating step, the suspension was sonicated for 5 min to disperse the particle substrates. The coating times for both PDADMA and silica nanoparticles were 20 min and the suspension was stirred using magnetic stirrer at 500 rpm. The excess polymer and silica nanoparticles were removed by three repeated centrifugation (4000 rpm, 10 min)/water wash/redispersion cycles. The deposition of subsequent multilayers was performed by repeating the procedure under the same conditions outlined above for the first deposition cycle. The core-shell materials were calcined at 550 °C for 1 day prior to characterization.

2. Conversion of the Properties of Core-Shell Particles to Porous Shells

Due to the size and nanoparticle packing density differences, the relative weight ratio of the core and shell of the core-shell particles are different as the number of layers changes. To better understand the effect of coating steps on the shell physical properties, we have calculated various shell properties of individual particles including total volume, pore volume, density etc. based on equations 1-5, which are used to remove the contribution from the nonporous cores from the measured values obtained for core-shell nanoparticles.

$$V_{c\text{-}s} = 4\pi R_{c\text{-}s}^3/3 \quad (V_c = 4\pi R_c^3/3) \tag{1}$$

$$ST = R_{c\text{-}s} - R_c \tag{2}$$

$$V_s = V_{c\text{-}s} - V_c \tag{3}$$

$$PV = 1/\rho_{c\text{-}s} - 1/\rho_c \tag{4}$$

$$\rho_{c\text{-}s} = (\rho_c V_c + \rho_s V_s)/V_{c\text{-}s} \tag{5}$$

In these equations, V, R and ρ are volume, radius, and density, respectively. Subscripts $c\text{-}s$, c, and s represent core-shell, core, and shell, respectively. ST and PV are the abbreviations of shell thickness and specific pore volume, respectively. The particle diameters were the average over ~150 particles obtained from the SEM images. Using equations (1) to (3) and assuming spherical particles, one can obtain the core and core-shell particle volumes (V_c and $V_{c\text{-}s}$), shell thickness (ST), and shell volume (V_s). The specific pore volumes of the core-shell particles were derived from the volume of adsorbed nitrogen at a relative pressure of approximately 0.99 (except for the particles with only one coating). The density of the nonporous silica core (ρ_c) is assumed to be 2.2 cm³/g. With these two values and using equations (4) and (5), one can then calculate the core-shell particle density ($\rho_{c\text{-}s}$) and shell density (ρ_s). After calculating the density and volume of shell and core-shell particles, we then determine the weight ratio of the shell and core-shell particle. This ratio multiplied by the sample weight is then used to adjust the sample weight for the nitrogen sorption analysis. After this conversion, we obtain a new set of information including isotherms, pore size distributions, and the physical properties of various shells with different coating layers.

3. Pore Size Distribution of Porous Shells

The pore size distributions (PSD) of representative silica shells, calculated from the desorption branches of the isotherms using the BHJ method, are displayed in Figure S1. The PSDs of the shells are centered around 10 nm (comparable to the nanoparticle building blocks) with a relatively broad pore size distribution, indicating a loose and random assembly of the nanoparticles and associated clusters in

the porous shells. Compared to the PSD of shells obtained after one coating relative to shells obtained from higher numbers of coatings, the sample with one coating shows a much high proportion of large pores with their diameters extending well beyond 30 nm. On the other hand, the PSDs of shells with three and five coatings are almost identical and almost all the pores range from 5 to 20 nm.
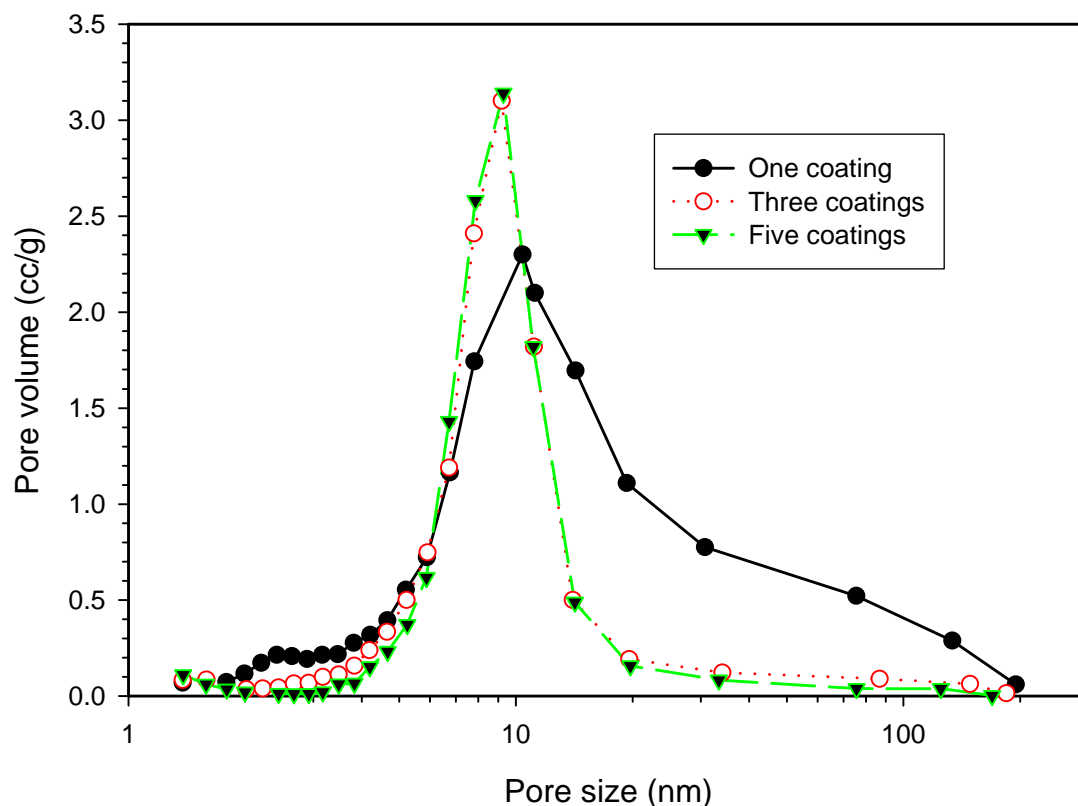

Figure S1. Pore size distributions (from desorption branches) of shells of one (●), three (○), and five (▼) coatings

4. Surface Area, Pore Volume, and Density of Porous Shells

Table S1 lists the shell surface area, pore volume, and density for shells obtained with different numbers of coatings. The surface areas of the shells are quite similar at ~ 400 m^2/g with the exception of the first coating, which has a large value of 533 m^2/g. Similarly, the first coated shell shows differences from the other shells in terms of density and pore volume.

Table S1. Nitrogen sorption data of porous silica shells[a]

Coating Number	Specific surface area (m^2/g)	Total pore volume (cc/g)	Density (g/cm^3)
1	533.9	1.36	0.553
2	421.5	0.93	0.724
3	400.7	0.89	0.743
4	396.7	0.89	0.741
5	408.0	0.86	0.760

a) Typical errors for surface area, pore volume and density are ± 2%.

5. Mechanical Stability of Porous Silica Shells

We have not conducted mechanical strength tests on our highly porous shells. However, unlike large NPs in the LBL process, where particle assembly and contact may be solely based on the weak electrostatic interactions between polyelectrolytes and particles and high temperature calcination is required to form necks (connectivity) between particles to improve mechanical stability, our ultrafine silica NPs appear to have lost their identify as individual particles and have formed extensive interconnections between particles during the assembly steps due to their highly reactive surfaces (high surface area and Si-OH density). The TEM image of the preformed silica NPs used in this work (Figure S2, panel A) clearly shows that these particles are connected during drying even without the need for polyelectrolyte gluing. After high temperature treatment, TEM imaging at high magnification (Figure S2 Panel B) indicated that there were large necks between the particles. The size of the particle necks is similar to the size of particles. It is well-known that increasing the size of the necks between particles is one of the most effective approaches to increase the mechanical strength of silica materials. Therefore, we expect our core-shell particles to be mechanically stable even though they are loosely packed. Indeed, the porous shells can survive long periods of sonication (to disperse the particles) before each coating step. Further experiments will be required to obtain quantitative information of the mechanical properties of our materials.
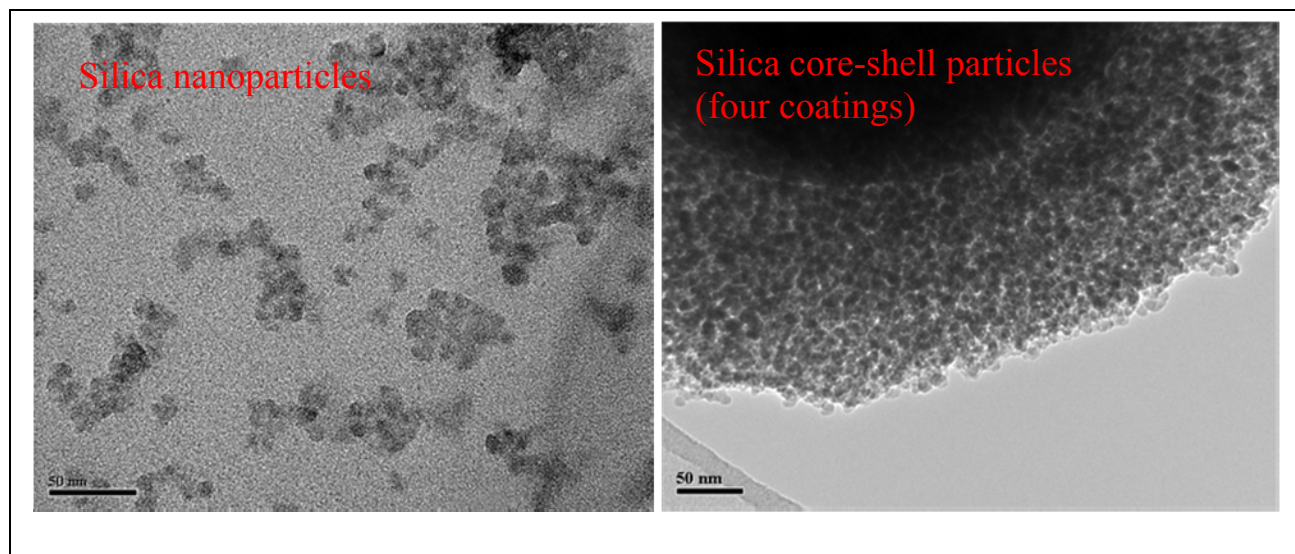
Figure S2. TEM images of silica nanoparticles and silica core-shell particles after four coatings.