SUPPORTING INFORMATION

Template-free synthesis of silica ellipsoids

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1. Experimental Section

1.1 Chemicals

Tetraethyl orthosilicate (TEOS, 98%) was obtained from Acros Organics; hexadecyltrimethylammonium bromide (CTAB, 99+ %) was purchased from Alfa Aesar; ethylene glycol, ReagentPlus ® (≥99%) was purchased from Sigma-Aldrich; Ammonium hydroxide (NH_4OH) was purchased from Pharmco products, Inc.; and ethyl alcohol 190 proof was obtained from Decon Labs, Inc. All reagents were used without further purification. Deionized water was used in all experiments.

1.2 Synthesis

A typical synthesis process was as follow: 50 mL of deionized water and 35 mL ethylene glycol (≥99%) were mixed; ~0.2525 g CTAB was dissolved in the prepared solvents and the mixture was vigorously stirred until clear; and then 0.842 mL ammonium hydroxide (1 M) was added. The total volume of the water and ethylene glycol was maintained at 85 ml for a series of predefined ratios. After 12 mL TEOS was slowly introduced, the reaction was held at room temperature with stirring. Following the reaction, the white precipitated was filtered, washed with 500 mL ethyl alcohol, and then dried overnight in air at ~60 ºC. Finally, the resultant white powder was calcination for 8 hrs at ~580 ºC to remove any residual CTAB, and represented the final product that was characterized as discussed below. The molar ratio of CTAB/NH_4OH/TEOS/ethylene glycol/water was 1:1.20:77.14:897.14:3968.57, when 50 mL water and 35 mL ethylene glycol were applied.

1.3 Characterization

Transmission electron microscopy (TEM, Zeiss EM 902 and JOEL JEM-2100) was performed to observe the size and the morphology of silica particles. To prepare the TEM samples, calcined silica white powders were dispersed in ethanol. A 10 µl aliquot of the silica-ethanol solution was dropped onto a carbon-coated copper grid. After evaporation of the ethanol, the sample was characterized by TEM at acceleration voltages of 80 and 200 kV.

The same preparation as above was used for the scanning electron microscopy measurements (using a SEM, Zeiss Supra 55 VP). For the SEM analysis, the voltage was 10 kV and the working distance was between 2 to 5 nm.

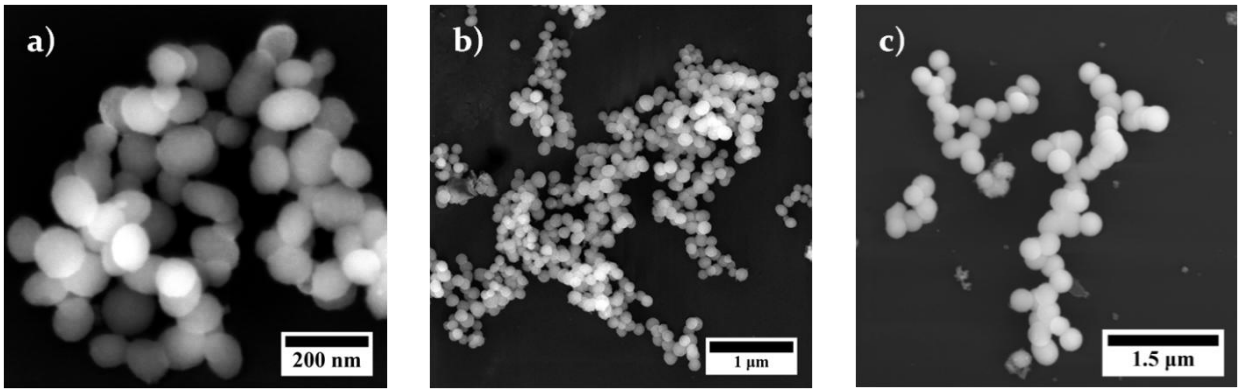
Fourier-transform infrared (FTIR) spectra were obtained in the range of 800-5000 cm-1 using a Varian 7000 spectrometer with a resolution of 2 cm^{-1}, and using a MIRacle single horizontal reflection Attenuated Total Reflectance (ATR) accessory.

Wide angle X-ray powder diffraction (XRD) measurements were performed using a PANalytic X-ray diffractometer in a 2θ range from 1° to 10°; graphite monochromatic CuKα (λ=1.54 Å) radiation was used with a nickel filter.

Nitrogen adsorption isotherms were measured using an ASAP 2010 analyzer (Micromeritics, Norcross, GA, USA) at -196 ^{o}C. Before the experiment, the samples were degassed at 120 °C to a constant pressure of 10^{-4} Torr. The isotherms were used to calculate the specific surface area, S_{BET}; micropore volume, V_{mic}; total pore volume, V_t; and pore size distribution. The micropore volume was calculated using Dubinin-Astakhov approach[1] and the total pore volume seen by the nitrogen molecules, from the last point of the isotherms based on the volume of nitrogen adsorbed; the volume of mesopores, V_{mes}, represents the difference between those two values. The relative microporosity was calculated as the ratio of the micropore volume to the total pore volume. Pore size distributions (PSDs) were determined using BJH method.[2]

2. Characterization

2.1 SEM



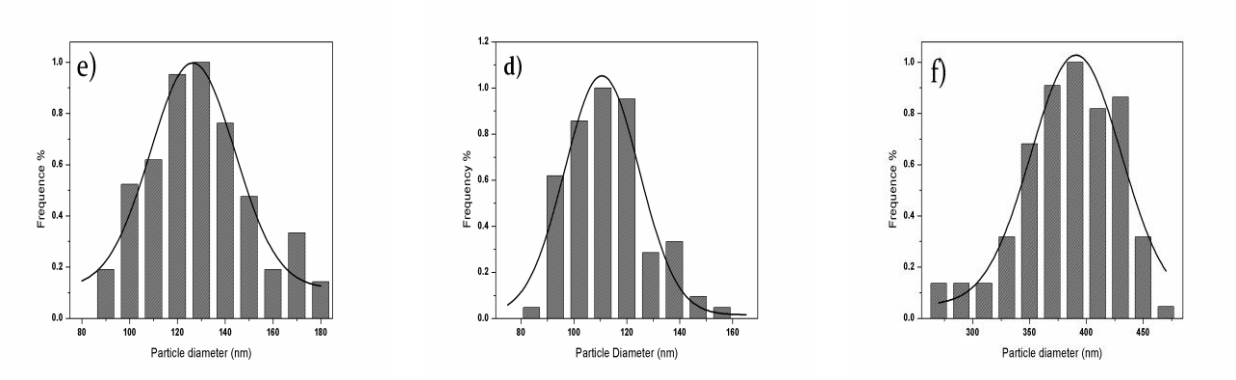


Figure S1: SEM images and particles size analysis of silica nanoparticles synthesized with different volume ratios of water to EG: (a) and (d), α = 1.43; (b) and (e), α = 0.89; (c) and f), α = 0.55.

The shapes of silica particles prepared with different volume ratios of water/ethylene glycol (α = 1.43, 0.89, and 0.55), as shown in SEM images, are provided in Fig. S1 (a), (b) and (c), respectively. From the SEM images, one can get approximate dimension of the particles: it is found that the mean long axis of silica ellipsoids is approximately 111 nm; and the diameters of the silica spheres are between 124 nm and 375nm. The particle size distribution graphs are given in panels (d), (e) and (f) of Fig. S1.

2.2 HRTEM

In Fig. S2, an HRTEM image allows determination of the approximate pore size of the porous silica ellipsoids for the sample prepare with α = 1.43. As shown in the figure, the diameter of the pore is estimated to be 3.0 nm; which is consistent with the result calculated from the nitrogen desorption/adsorption isotherm using the BJH method (see Fig S6 below).

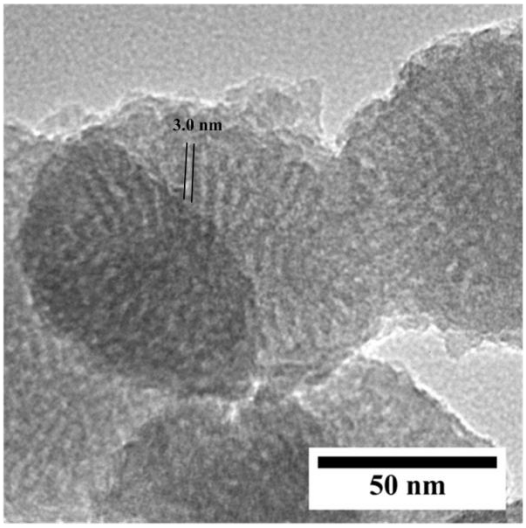


Figure S2: HRTEM image of mesoporous ellipsoidal silica (volume ratio of water/EG α = 1.43).

2.3 FTIR-ATR

Fig S3 provides the FTIR-ATR spectra for various silica particles prepared under different syntheses. Similar features are found: the intense band at ca. 1100 cm^{-1} is attributed to the transverse-optical mode of the Si-O-Si lattice. Absorption bands associated with the C-H bending vibrations were found between 1350 and 1500 cm^{-1} and between 2850 and 3000 cm^{-1}.[3] It is inferred that, although resultant silica particles have different morphologies, no different chemicals species are formed during reactions.

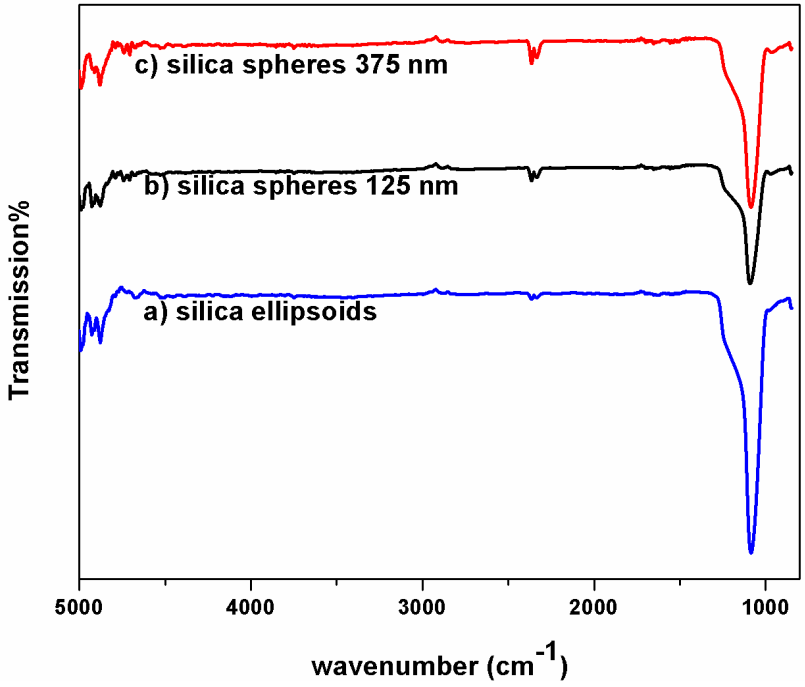


Figure S3: FTIR-ATR spectra of silica particles synthesized with different volume ratios of water to EG: (a) α = 1.43; (b) α = 0.89; and (c) α = 0.55.

2.4 XRD

Figure S4 below shows X-ray diffraction patterns of silica powders prepared using different volume ratios of water and EG. The three samples exhibited a single broad reflection (100), which corresponds to the average pore-pore correlation distance in the small angle region (θ = 1-8).[4] The patterns indicate that the silica products are mesoporous structures. The patterns show that the reflection intensity of spherical silica (curves (a) and (b)) is higher than that of the ellipsoidal silica (curve (c)), also that the reflection intensity increases with gradually decreasing of the volume ratios of water to EG, supporting the view that for the high ratio synthesis (α = 1.43), anisotopic surface tension forces are exerted on the nuclei, and the micelles generated by CTAB are altered, with the long range order of mesoporous silica decreased.

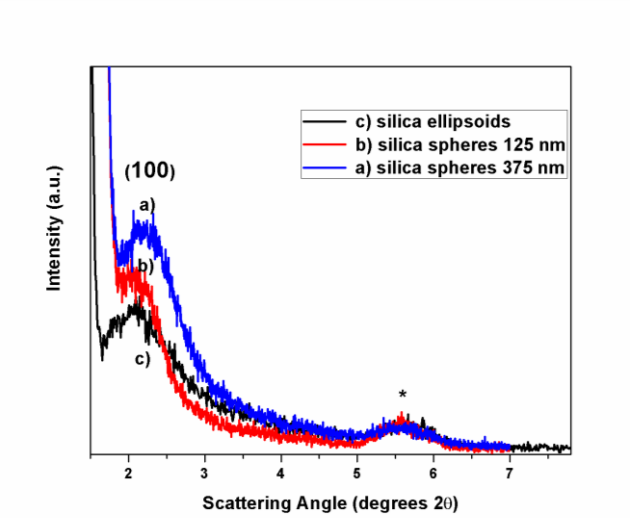


Figure S4: X-ray diffraction patterns of mesoporous silica ellipsoids and silica spheres formed in water-ethylene glycol volume ratios of (a) α = 0.55; (b) α = 0.89; and (c) α = 1.43. (Note: * labels an instrument intrinsic peak that always appears.)

2.5 Nitrogen Isotherm and PSDs

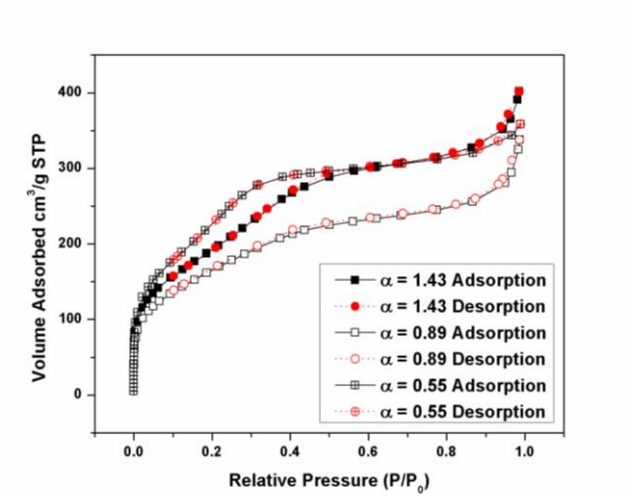


Figure S5: The nitrogen adsorption isotherms of varies morphologies of silica products.

Interestingly, for all three samples, no hysteresis was observed. This suggested that the particles are agglomerated close to one another and the conical wedges between particles can be considered as the most likely predominate shape. The average pore size based on the BJH distribution (Fig. S6) is shown to be less than 10 % the particle diameter for silica spheres (α = 0.55 and 0.89) and about 30% for the silica ellipsoids (α = 1.43). This difference, once again is linked to the shapes of the particles and their packing/agglomeration in the solids. The pore size of silica ellipsoids is supported by HRTEM measurement (Fig. S2).

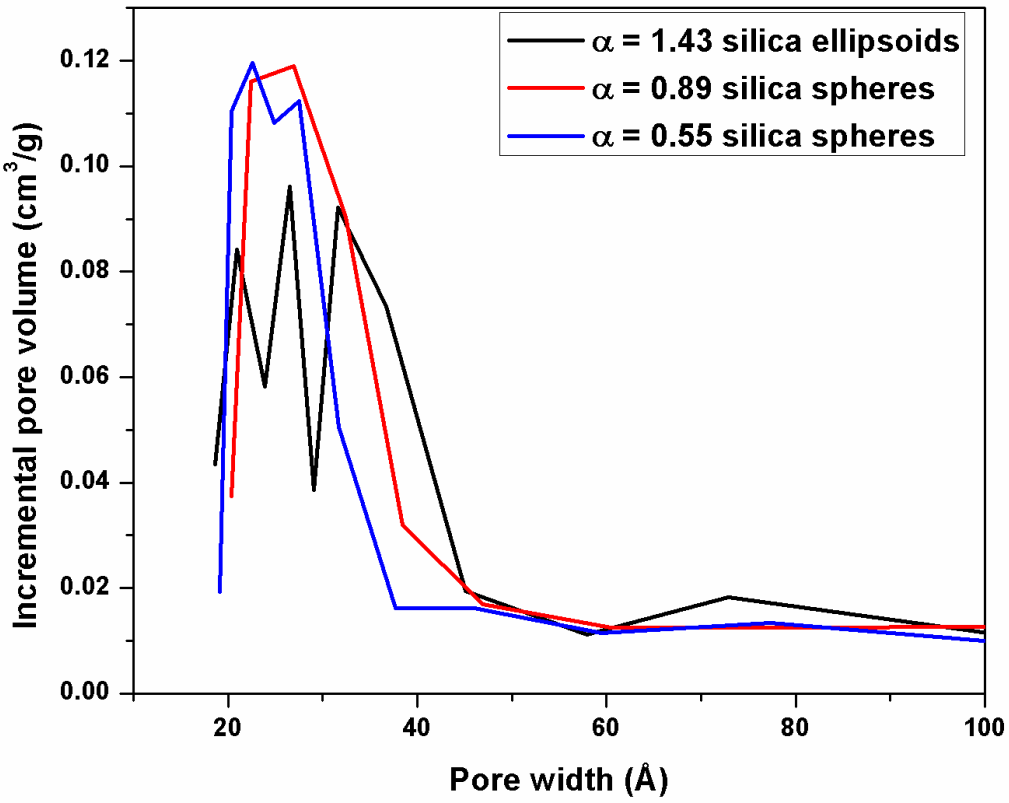


Figure S6: Pore size distribution for silica products.

3. Reference

1. M. M. Dubinin, *Porous structure and adsorption properties of active carbons*; P. L. Walker, Jr., Ed.; Marcel Dekker: New York, 1966, **2**, 51
2. S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area, and Porosity*, Academic Press, New York, 1982.
3. S. Bruynooghe, F. Bertin, A. Chabli, J. C. Gay, B. Blanchard and M. Couchaud, *Thin Solid Films*, 1998, **313**, 722.
4. D. Y. Zhao, J. L. Feng, Q. S. Huo, N. Melosh, G. H. Fredrickson, B. F. Chmelka and G. D. Stucky, *Science*, 1998, **279**, 548.