Electronic Supplementary Information

Double Function of Tris(hydroxymethyl)aminomethane (THAM) for the Preparation of Colloidal Silica Nanospheres and the Conversion to Ordered Mesoporous Carbon

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Experimental

Preparation of colloidal silica nanospheres: THAM (99%, Wako Pure Chemical Ind. Ltd.) was dissolved in deionized water with stirring at certain temperatures described below. Tetraethoxysilane (TEOS, Wako Pure Chemical Ind. Ltd.) was added to the aqueous solution of THAM with stirring. The mixtures were stirred at specified temperatures for 24h.

Synthetic temperature: The molar ratio of the mixture was set at 23 TEOS: 5 THAM: 1390 H_2O. The synthetic temperature was varied at 40 ^oC, 60 ^oC, and 80 ^oC, and the samples are denoted as C40, C60, and C80, respectively. The variation in the pH values of an aqueous solution of pure THAM (0.2 M, the concentration is equivalent to the molar ratio above) with temperature was measured.

Concentration of TEOS: The molar ratios of the mixture were set at x TEOS: 5 THAM: 1390 H_2O. The value of x was 9, 23, 33, 45, and 90, and the products are denoted as S9, S23, S33, S45, and S90, respectively. The synthesis temperature was 60 ^oC.

Concentration of THAM: The molar ratios of the mixture were set at 23 TEOS: y THAM: 1390 H_2O, where y = 1.3, 2.7, 10, 20, and 40. The products are denoted as T1.3, T2.7, T10, T20, and T40, respectively. The synthesis temperature was 60 ^oC.

Preparation of colloidal silica nanospheres with a different molar ratio for comparison: One sample was synthesized by the same molar ratio (but THAM instead of lysine) as that reported by Yokoi *et al*.[1] The molar ratio of the mixture was set at 50 TEOS: 1 THAM: 7720 H_2O. This colloidal silica nanospheres are denoted as L1.

Synthesis of mesoporous carbon: A colloidal silica aqueous solution (10 mL), prepared at 60 ^oC from the starting solution composed of 90 TEOS: 50 THAM: 1390 H_2O, was evaporated at 60 ^oC to form a white thick plate. Subsequently, 0.3 mL of H_2SO_4 and 2 mL of H_2O were added to infiltrate into the plate. The mixture was dried in an oven at 60 ^{o}C for 1 day and then the plate was heat-treated at 100 ^{o}C for 2h to evaporate water completely. The sample was then treated at 150 ^{o}C for polymerization of THAM. The color of the sample changed from white to brown. The carbonization was completed by heating the pulverized black brown sample at 900 ^{o}C for 6 h under a N_2 flow. The formed carbon-silica composite was treated with a mixture of 2 mL HF, 10 mL H_2O, and 10 mL ethanol. In our FT-IR and Raman spectroscopic results of the mesoporous carbon, we did not find the presence of remaining silica. The amount should be at least under the detection limit of these techniques. The silica-free carbon was washed with water and ethanol and dried under vacuum.

Characterization: HRSEM images were taken with a Hitachi S-5500 electron microscope at an accelerating voltage of 30 kV. XRD measurement was performed on a Rigaku-Rint-Ultima III powder diffractometer with Cu Kα radiation (40 kV, 40 mA) by using parallel beam geometry equipped with a parabolic multilayer solar slit. The thermogravimetry (TG) measurement was carried out with a Rigaku Thermo Plus 2 instrument under a dry air flow at a heating rate of 10 ^{o}C min^{-1}. Nitrogen adsorption desorption measurements were performed on an Autosorb 1 instrument (Quantachrome Instruments) at 77 K. Samples were preheated at 120 ^{o}C for 3h under 1 x 10^{-2} Torr prior to the measurements. The pore size distributions were evaluated by the BJH method using adsorption branches. Specific surface areas were calculated by the BET method. The total pore volumes were evaluated from the amount adsorbed at a relative pressure (P/Po) of about 0.99. Solid-state ^{29}Si MAS NMR spectra were recorded on a JEOL JNM-ECX-400 spectrometer at a resonance frequency of 79.42 MHz with 90 ° pulse and a recycle delay of 400 s by using a 4 mm zirconia rotor and spinning at 5 kHz. It was confirmed that the signals were fully relaxed under these conditions so that quantitative analysis is possible. The amounts of organic constituents were determined by CHN analysis (Perkin-Elmer, 2400 Series II).

Reference

1 T. Yokoi, Y. Sakamoto, O. Terasaki, Y. Kubota, T. Okubo, T. Tatsumi, *J. Am. Chem. Soc*. 2006, **128**, 13664

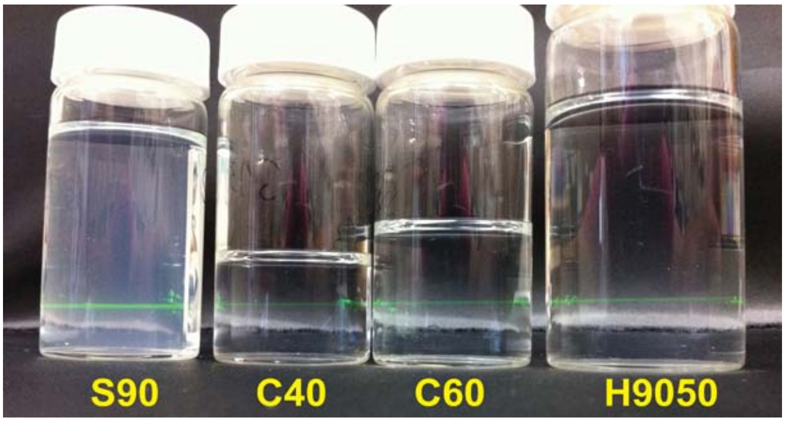

Figure S1 Images of Tyndall phenomena of aqueous solutions of colloidal silica nanospheres.

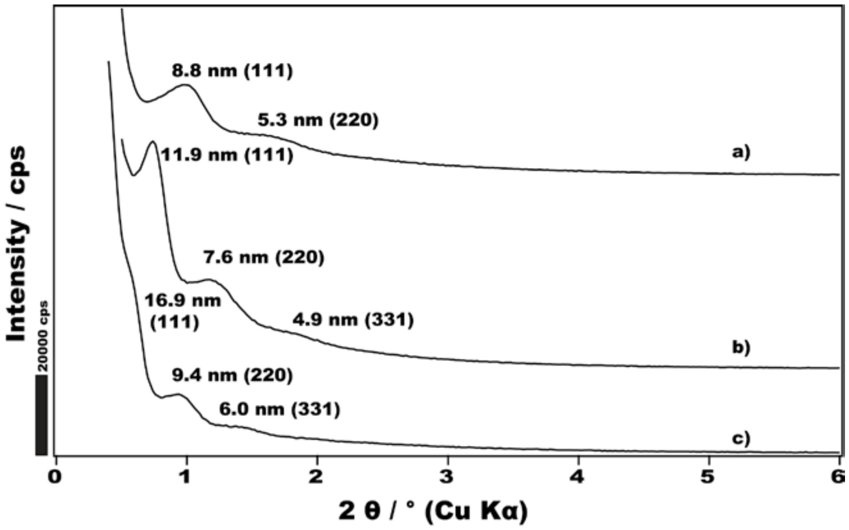

Figure S2 XRD patterns of a) C40, b) C60, and c) C80 after calcination at 550 ^{o}C.

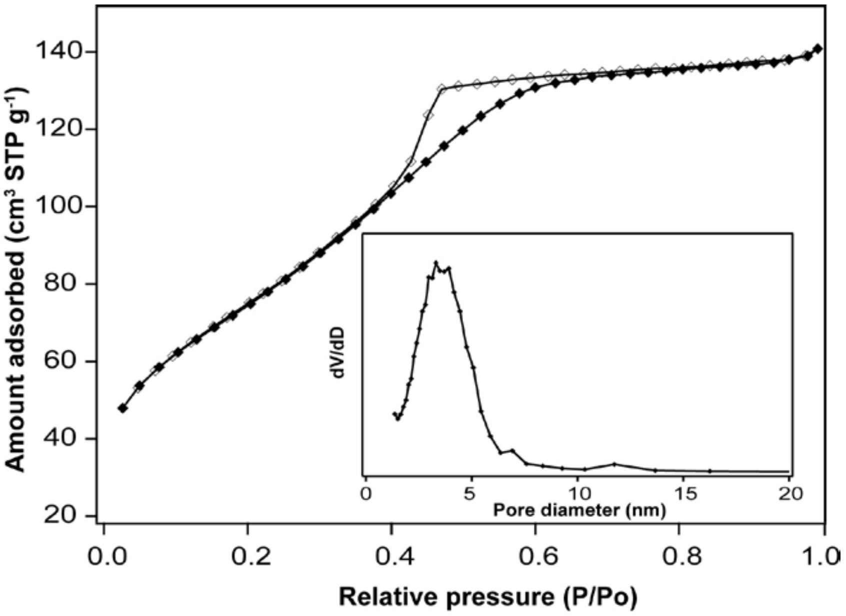

Figure S3 N_2 adsorption-desorption isotherm of silica nanospheres (C60). Inset: pore size distribution derived from the adsorption branch (BJH method).

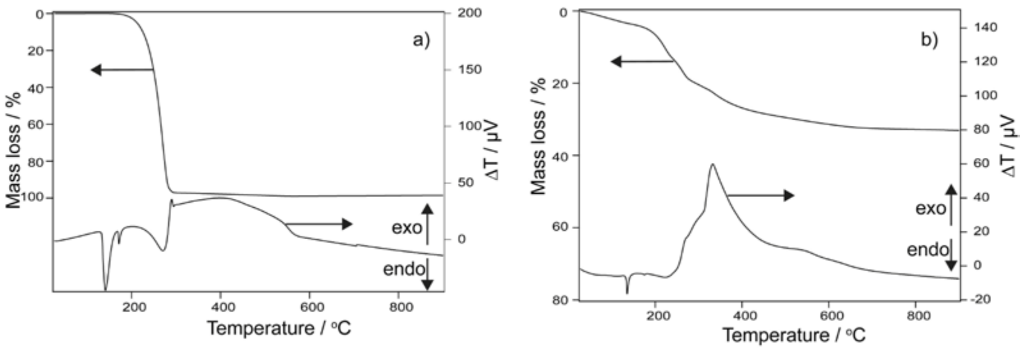

Figure S4 TG-DTA curves of a) THAM and b) silica nanospheres (C60) before calcination.

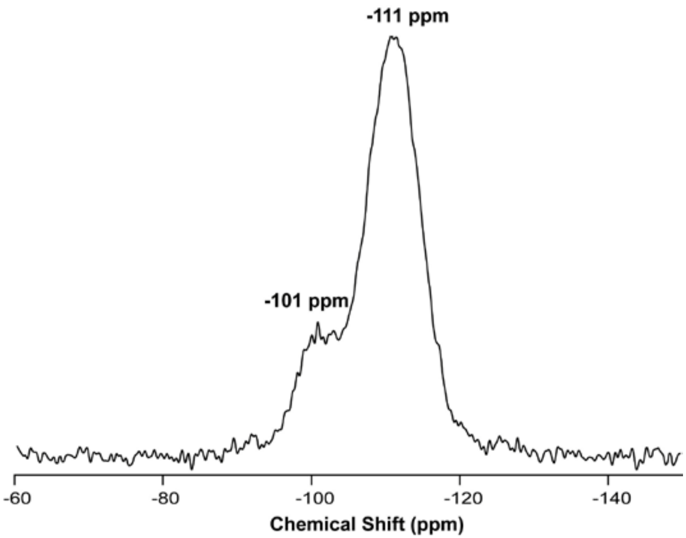

Figure S5 Solid-state ^{29}Si MAS NMR spectrum of C60.

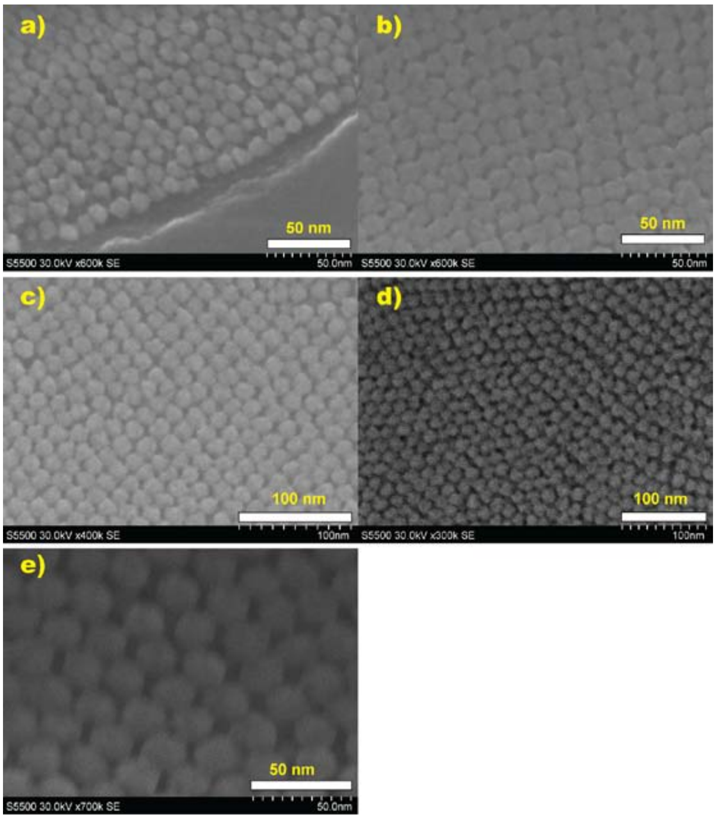

Figure S6 SEM images of a) S9, b) S23, c) S33, d) S45, and e) S90.

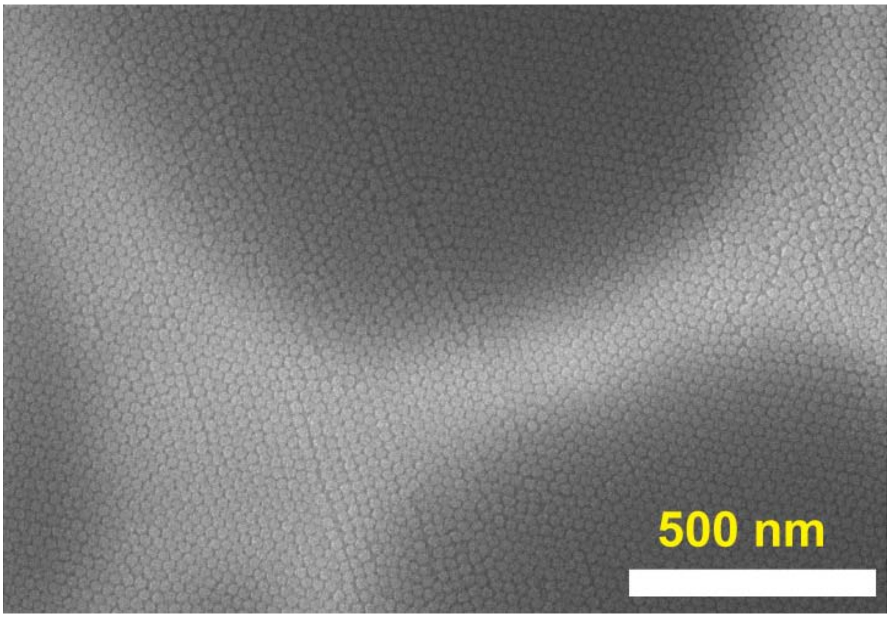

Figure S7 SEM image of colloidal silica nanospheres (S90).

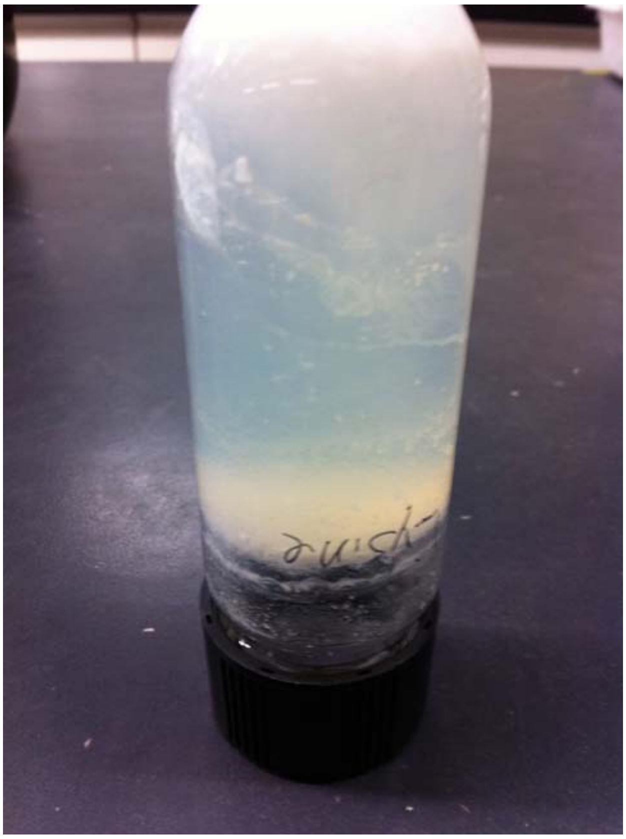

Figure S8 Picture of colloidal silica product in the case of lysine as a catalyst.

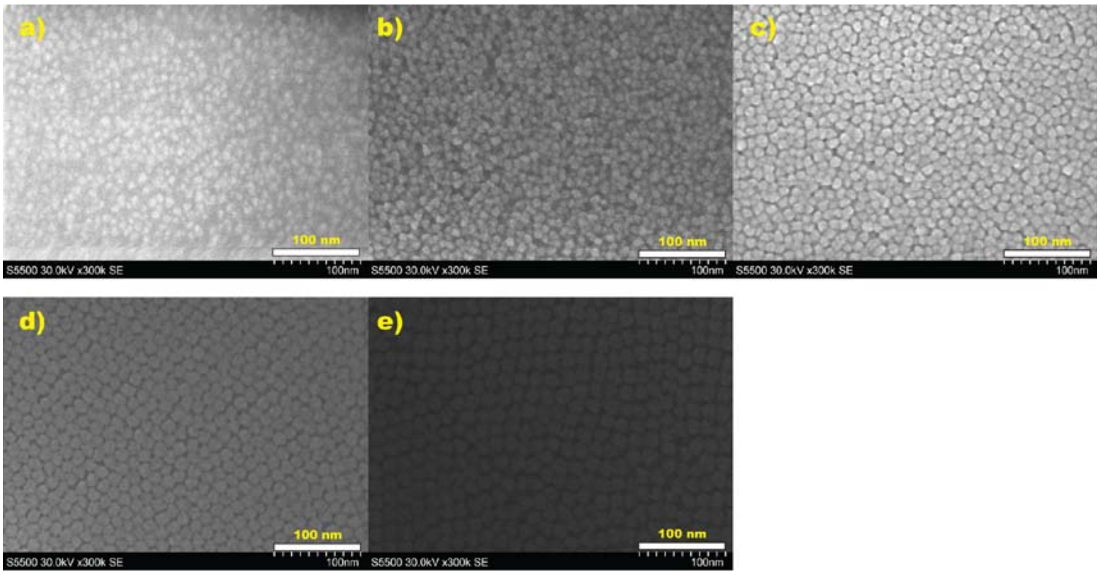

Figure S9 SEM images of a) T40, b) T20, c) T10, d) T2.7, and e) T1.3.

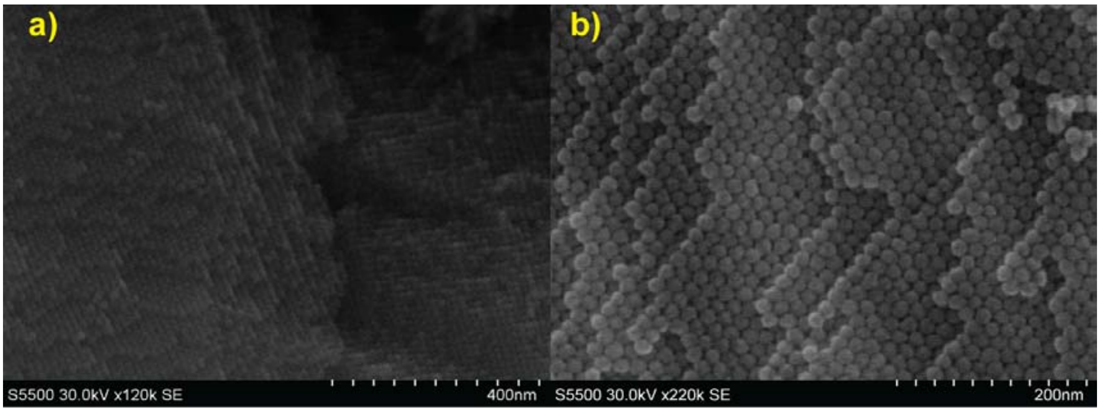

Figure S10 SEM images of silica nanospheres of a) L1 after evaporation at 60 °C and b) C80 after calcination at 550 °C.

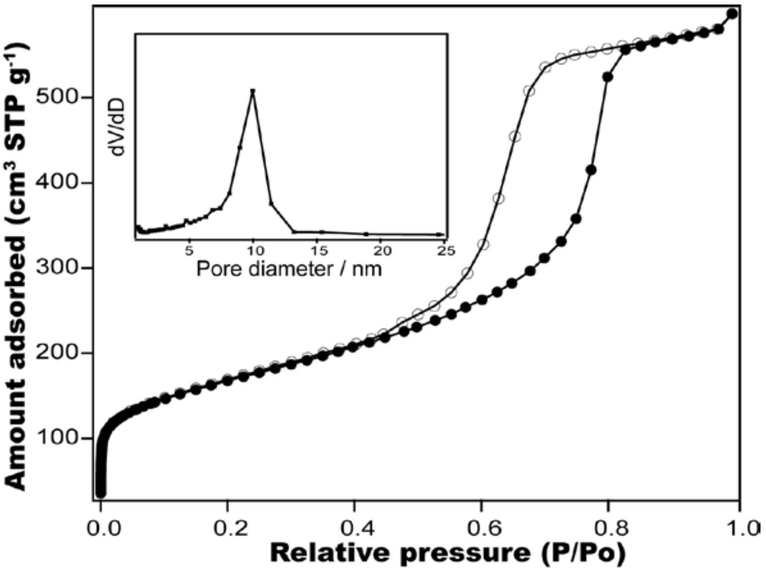

Figure S11 N_2 adsorption-desorption isotherm of mesoporous carbon. Inset: pore size distribution of mesoporous carbon (BJH method).