Supporting Information

Collapsed (Kippah) Hollow Silica Nanoparticles

*Kun-Che Kao, Chieh-Jui Tsou and Chung-Yuan Mou**

Experimental Section

Materials:

Reagents: Cetyltrimethylammonium bromide (CTAB, 99%+), tetraethyl orthosilicate (TEOS, 98%), decane, dodecane, and hexadecane (99%+) were obtained from Acrös. Ammonia solution (35 wt%), ethanol (99%) and hydrogen chloride (36 wt%) were purchased from Fisher Scientific. All reagents were used as received without further purification.

Synthesis of alkane added MSNs: Alkane added mesoporous silica nanoparticles (C10-MSN, C12-MSN, and C16-K-MSN) were synthesized using an oil-in-water microemulsion system with CTAB as the surfactant. The reaction mixture was prepared in the following molar ratios: 0.36 CTAB / 1.0 TEOS / 244 ethanol / 3653 H_2O / 11 NH_3 / 2.1 alkane (decane, dodecane, and hexadecane). Initially, 0.193 g of CTAB was dissolved in 98 g of water, and the alkane/ethanol solution was added into the mixture under stirring at 50^oC. After that, 0.77 g of 35 wt% NH_3 was added to reach a pH value of about 11.5, and the mixture was stirred at 50^oC for 20 minutes.

Then, 1.67 ml of 20% TEOS/ethanol (concentrated TEOS) solution was added into the mixture under stirring, and the whole solution was further stirred at 50°C for 20 hours. After reaction, as-synthesized solutions were centrifuged to isolate the meseporous silica products. The precipitates were washed with ethanol four times with sonication to remove un-reacted chemicals. To remove the surfactant templates, the particles were dispersed in HCl/ethanol (2 g/50 ml) solution and refluxed at 80°C for 20 hours. Finally, the products were washed with ethanol and dried at 60°C for 16 hours.

Synthesis of C16-H-MSN (hexadecane): C16-H-MSN was synthesized by separating nuclei formation and particle growth into two steps. 1.67 ml of 4.7% TEOS/ethanol (diluted TEOS) solution was firstly added into the same molar ratio solution of CTAB/H_2O/hexadecane/ethanol/NH_3 mentioned above. The mixture was stirred at 50°C for 4 hours. Then, 1.67 ml of 20% TEOS/ethanol solution was added into the solution. The other steps were the same as in the procedure for synthesizing the alkane added MSNs.

Characterization:

TEM analysis was performed on a transmission electron microscope (Hitachi H-7100) operated at 100 kV. Samples dispersed in ethanol were deposited on a carbon-coated Cu grid and dried under air atmosphere. N_2 adsorption-desorption isotherms were

collected on a Micrometric ASAP 2010 apparatus at 77 K under continuous adsorption conditions. Samples were degassed at 10^{-3} Torr at 110^{o}C for 16 h prior to the experiments. The pore volume and pore size distribution plots were obtained from the analysis of the adsorption or desorption isotherms using the BJH (Barrett–Joyner–Halenda) method. Single point total pore volumes were measured at P/P_0~0.99, and mesopore volumes were obtained from BJH adsorption cumulative volume of pores between 1.0 nm and 15 nm. Samples' surface areas were obtained through BET (Brunauer – Emmett – Teller) analysis. Scanning electron microscope (SEM) images were recorded on JSM-7600 (field-emission JEOL).

Supplementary figures:

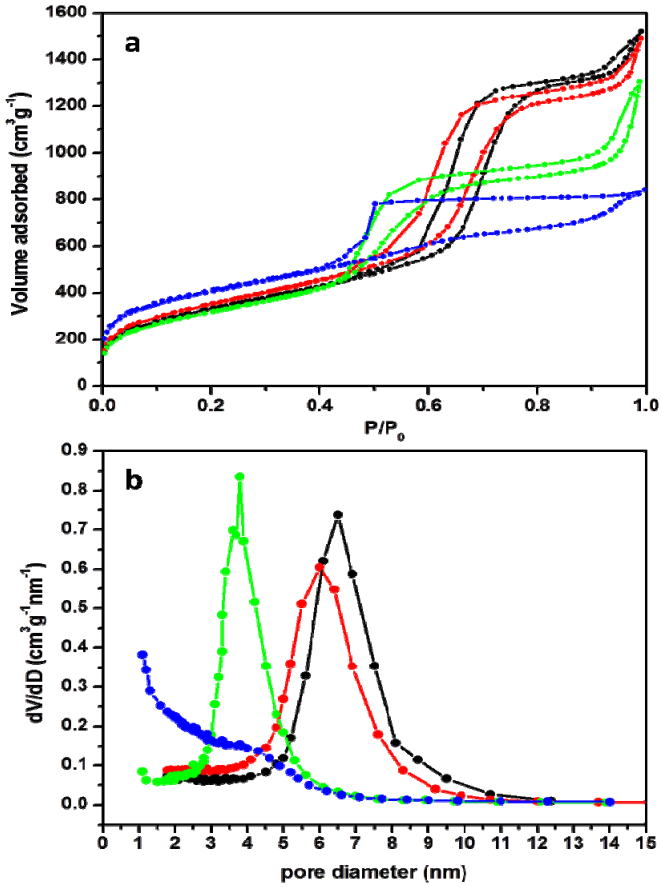

Figure S1. Nitrogen adsorption-desorption isotherms (a) and corresponding pore size distribution plots (b) of C10-MSN (black), C12-MSN (red), C16-K-MSN (blue), and C16-H-MSN (green).

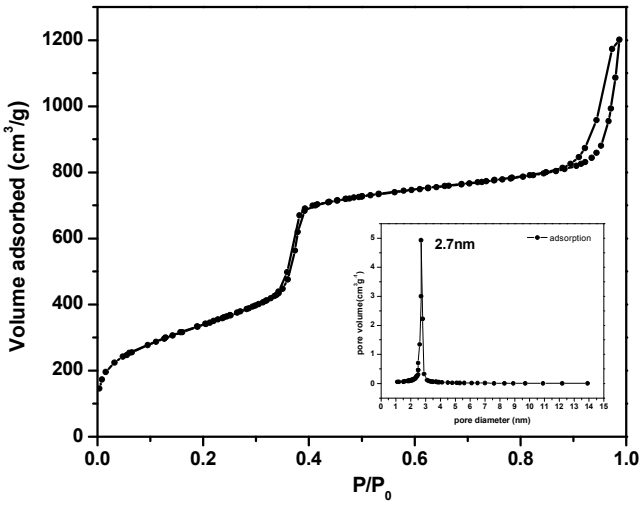

Figure S2. Nitrogen adsorption-desorption isotherms of conv-MSN which was synthesized without any alkane. (Inset: pore size distribution derived from the isotherm of adsorption branch).

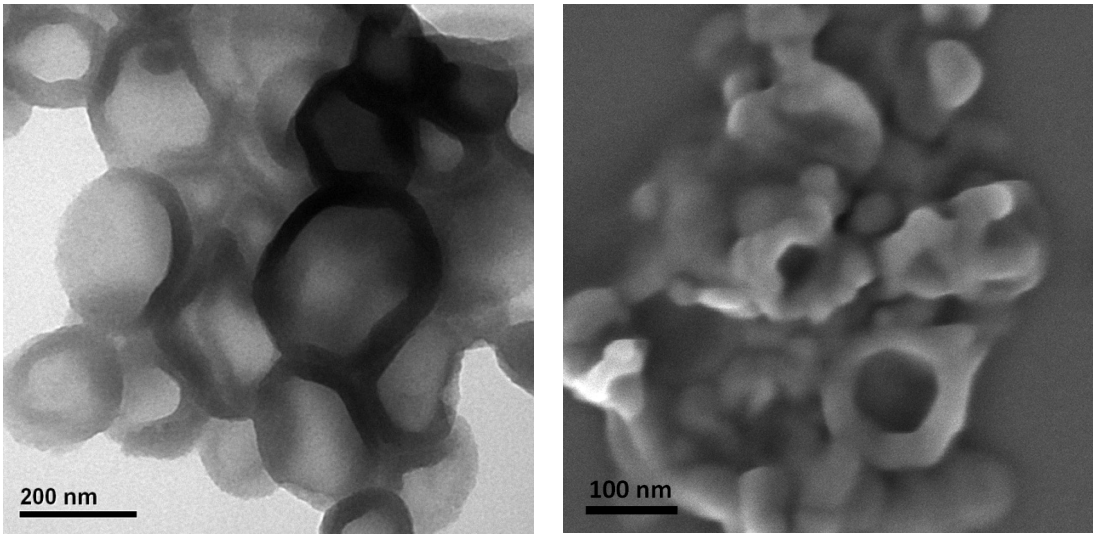

Figure S3. TEM and SEM iamges of C16-KMSN in the initial stage of reaction. The paritcles were collected by centrifuging 3 minutes after concentrated TEOS was added into the CTAB/hexadecane/NH_4OH solution. In SEM picture, some collapsed kippah-like structure could be clearly seen but many other was not formed yet.

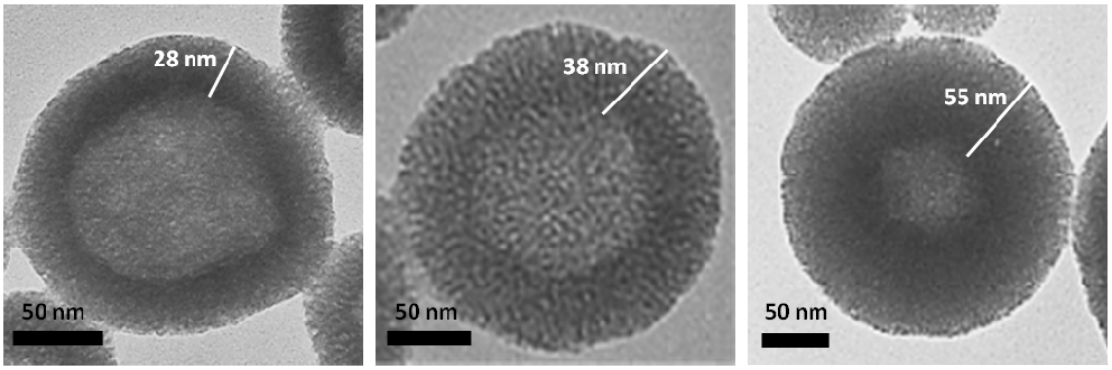

Figure S4. TEM images of C16-H-MSNs with different thickness of silica shells controlled by increasing the amount of TEOS.

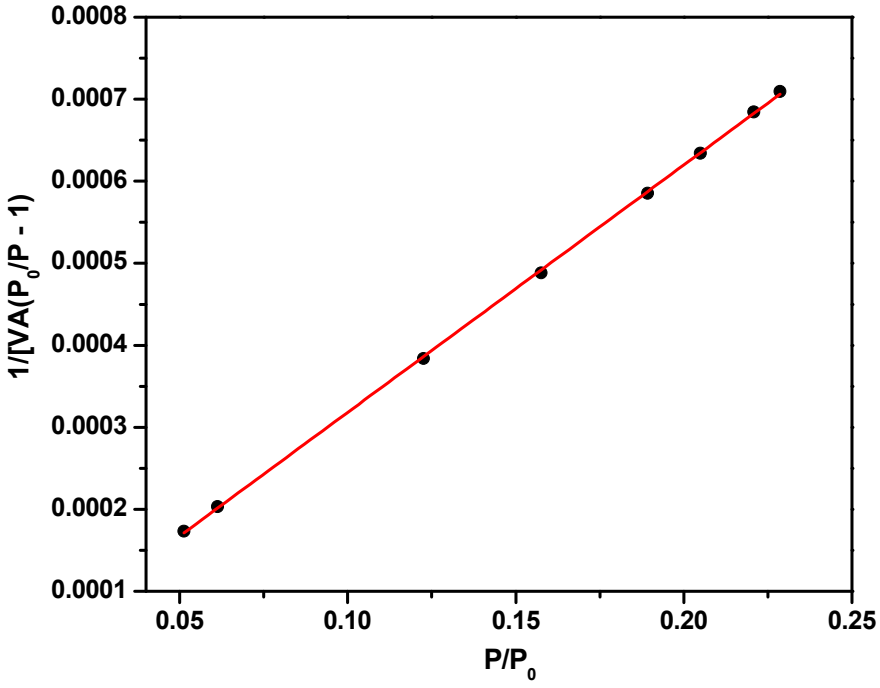

Figure S5. BET plot of C16-K-MSN with P/P_0 ranged from 0.051 to 0.229. This plot shows the accuracy in determining the surface area (1439 m^2/g as in Table 1). Even when delete two data points at high end of P, the surface area remains essentially the same.

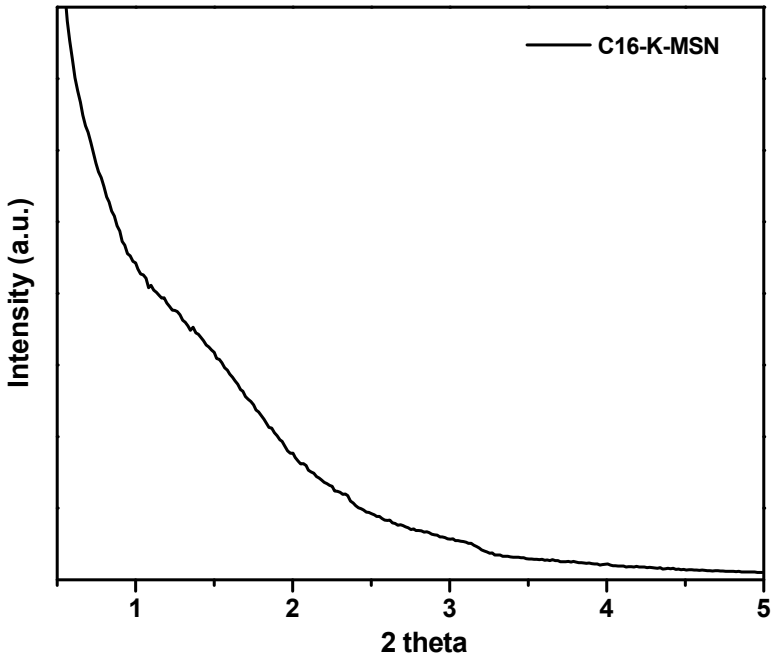

Figure S6. Powder X-ray diffraction pattern of C16-K-MSN. It shows a highly disordered mesostructure.