Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

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S1. Experimental

S1.1. Materials

Methyltrimethoxysilane (MTMS, 95%) and ethyltrimethoxysilane (ETMS, 98 %) were purchased from Aldrich Chemical and used without further purification. Ammonium hydroxide solution (30 wt% as NH_3) was obtained from Sam-Chun Chemicals and used as a catalyst. Methyl alcohol (MeOH, 99.5%, Sam-Chun Chemicals,) and Ethyl alcohol (EtOH, 95%, Sam-Chun Chemicals) were used as a solvent, respectively.

S1.2. Preparations of self assembled cubic silsesquioxane crystals

a) T_8^{methyl} silsesquioxane cubic crystals

Three different reaction conditions, used in the preparation, were shown in Table S1.

(Case 1)

To a round bottom flask with a magnetic stirrer were placed 270 ml of ethyl alcohol and NH_4OH (30wt %, 27 ml, 208 mmol). Methyltrimethoxysilane (98 %, 0.75 ml, 5.4 mmol, MTMS) was added to a basic alcohol solution and the resulting solution was stirred at room temperature for 12 hrs. The initially clear solution became turbid after 2 hours and the stable suspension was maintained up to 12 hours of stirring. The products were started to precipitate after 12 hours, resulting a clearer supernatant. After 48 hours of further stirring, the resulting solution was filtered using a membrane filter and the product was washed several times with ethyl alcohol. 0.081 g MTMS based cubic crystals (yield, 10.8%) was obtained after drying in a vacuum oven at 70 °C for 2 hrs.

In order to investigate the colloidal self assembly growth process, the reaction was quenched by stopping the stirring and several aliquots of sample were taken after different aging times.

After 0, 2, and 6 hours of aging, the supernatant of resulting suspension was taken and 0.1 ml of each aliquot was dropped to a cupper substrate using a syringe and dried at room temperature for 1 hour. For final product (cubic crystals), the sample was taken from the precipitates after aging 48 hours. The substrates for electron microscope analyses were shown in below.

Substrate for SEM analysis	Substrate for TEM analysis
Non-coated Cu grids were purchased from Tedpella, Inc.	Cu grids coated with formvar and carbon were purchased from Tedpella, Inc.

(Case 2 and 3)

To a round bottom flask with a magnetic stirrer were placed 270 ml of ethyl alcohol and NH_4OH (30wt %, 27 ml, 208 mmol). Methyltrimethoxysilane (98 %, 0.75 ml, 5.4 mmol, MTMS) was added to a basic alcohol solution and the resulting solution was stirred at 60 ^oC for 8 hours (or heated in an auto-clave at 100 ^oC for 1 hour). The precipitated powders were collected using a membrane filter and washed several times with ethyl alcohol. 0.085 g MTMS based cubic crystals (yield, 11.2% for both cases) was obtained after drying in a vacuum oven at 70 °C for 2 hrs.

Table S1. Reaction conditions for the preparation of T_8^{methyl} silsesquioxane crystals.

	unit	Case 1 (flask)	Case 2 (flask)	Case 3 (auto-clave)
EtOH	ml	270	270	270
NH_4OH (30 wt %)	ml	27	27	27
methyltrimethoxysilane	mmol	5.4	5.4	5.4
Temperature	℃	30	60	100
Reaction time	hrs	48	8	1

b) T_8^{ethyl} silsesquioxane powders

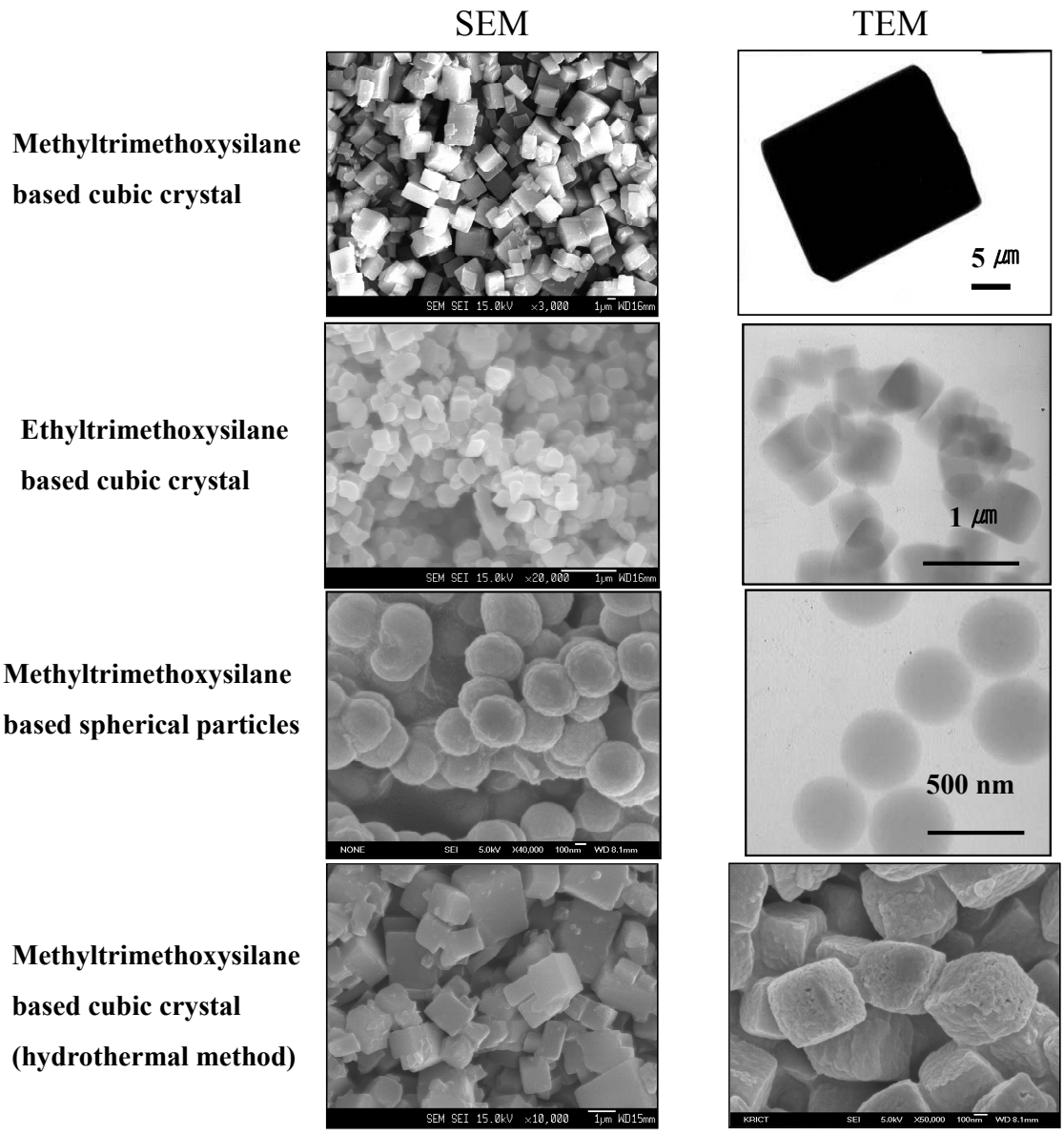
To a round bottom flask with a magnetic stirrer were placed 270 ml of ethyl alcohol and NH_4OH (30 wt%, 27 ml, 208 mmol). Ethyltrimethoxysilane (98 %, 0.75 ml, 4.6 mmol, ETMS) was added to a basic alcohol solution. The reaction mixture was stirred at 60 ^oC for 6 hrs, maintaining a clear solution. Deionized water (100 ml) was added to induce the precipitation. The suspension was filtered through a membrane filter and the product was washed with ethyl alcohol several times. 0.047 g of ETMS based powders (yield, 6.05%) was obtained after drying in a vacuum oven at 70 °C for 2 hrs.

S1.3. Characterization

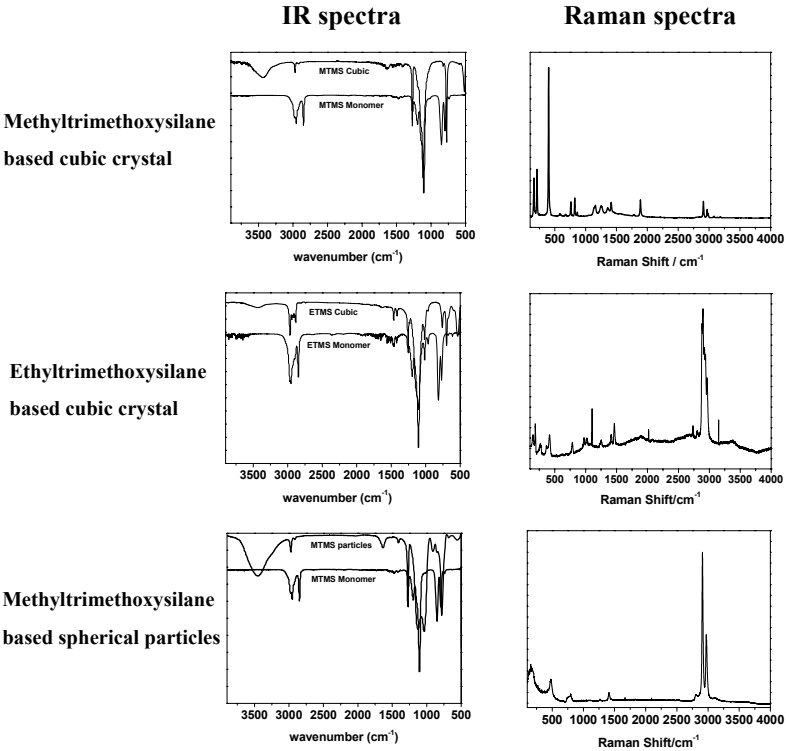
The thermal analyses of the products were performed with the thermo-gravimetric analyzer (TGA, Perkin-Elmer). The Fourier transform infrared spectrometer (FT-IR, AAB FTLA2000) and Raman spectrometer (JASCO, NRS-3100) were used for the chemical characterization. X-Ray powder diffractometer (XRD, Rigaku, D/RAD-C diffratometer with Cu Kα radiation) was

used to investigate the structures of products. The sizes and morphologies of self assembled products were examined with field emission scanning electron microscope (FE-SEM, JEOL JEM-6340F) and transmission electron microscope (TEM, JEOL EM-2000EXII)

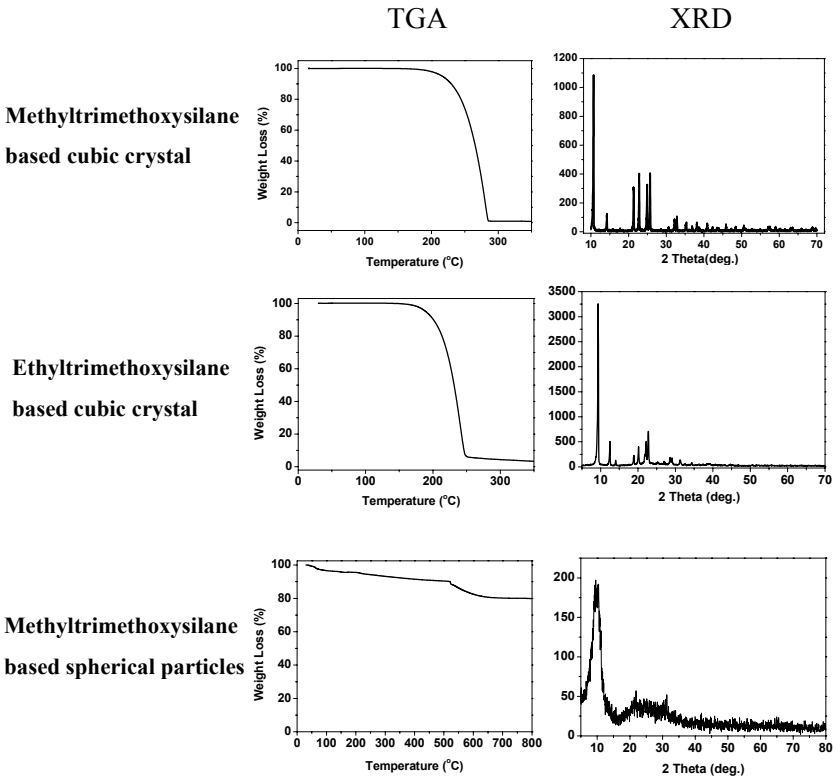
S2. Electron microscope images for T_8^{methyl}, T_8^{ethyl} silsesquioxane crystals and MTMS powders



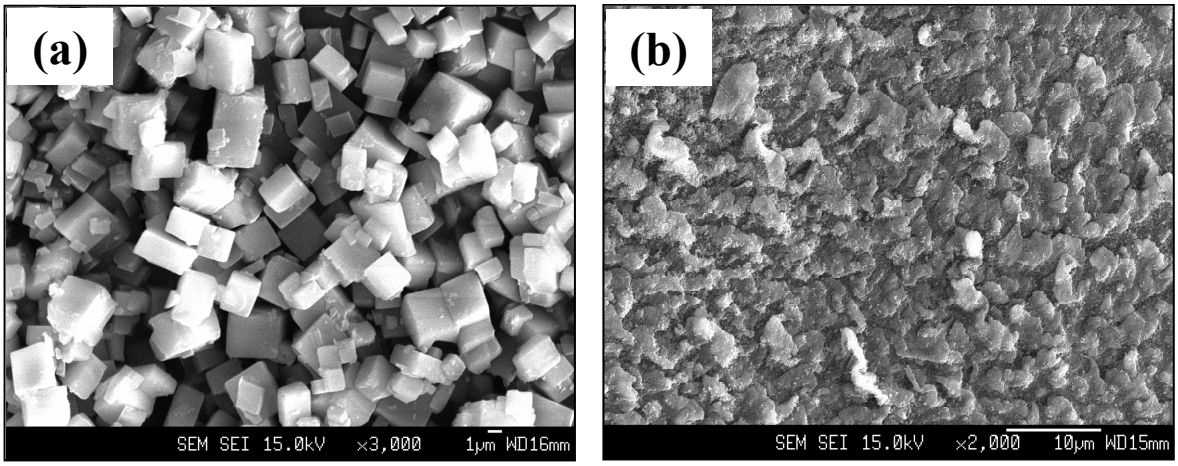
S3. IR and Raman spectra for T_8^{methyl}, T_8^{ethyl} silsesquioxane crystals and MTMS powders



S4. TGA and XRD patterns for T_8^{methyl}, T_8^{ethyl} silsesquioxane crystals and MTMS powders



S5. The SEM images of T_8^{methyl} silsesquioxane cubic crystals before (a) and after (b) heat treatment (200 ^oC).



S6. TG-IR result for T_8^{methyl} silsesquioxane cubic crystals**.**