Supplementary Material (ESI) for Chemical Communications

Synthesis of coesite nanocrystals from ethane bridged periodic mesoporous organosilica at low temperature and extreme pressure

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Experimental:

Synthesis of Et-PMO:

Materials: Bis(triethoxysilyl) ethane (BTSE) was purchased from Gelest Inc., USA, 1-hexadecyl- trimethylammoniumbromide (CTAB) from Alfa Aesar. All the chemicals were used as received without any purification.

The sonicator used in the present research was Cavitator Ultrasonic ME 11 (Mettler Electronics, USA) with a maximum power output of 200 W at 67 kHz.

Synthesis: A base catalyzed surfactant-templating sonochemical method was used for the synthesis of the periodic mesoporous organosilica (PMO) material with ethane bridging group designated as Et-PMO. In a typical synthesis, 1.65 g of CTAB was dissolved in a mixture of 10.8 g NH_4OH (35 wt %) and 19.8 g de-ionized water. To the above solution, 7.5 mmol of BTSE was added drop wise (within about 1 min). The reaction mixture was sonicated for 30 min at room temperature. The precipitated Et-PMO was then filtered, washed with distilled water and dried in vacuum. The total yield was about 2.5-2.6 g. The extraction of the template was carried out by sonicating the as–synthesized powder in a mixture of 75 g of acetone and 7.5 g of 2N HCl for another 30 min. The powders were collected by filtration.

Multi-anvil experiment:

The experiments were carried out in a multi-anvil assembly with a 1500 t hydraulic press. The samples were placed inside a 14/8 Cr_2O_3 doped MgO octahedron lined with a cylindrical Rhenium furnace having a diameter of 6.3 mm. The Rhenium furnace served as a capsule for the periodic mesoporous organosilica simultaneously. The octahedron was closed with MgO end caps. A Pt/Re thermocouple was used to determine the temperature. The thermocouple was fed through the MgO end pieces and was in direct contact with the sample. The octahedron was placed between eight corner-truncated tungsten carbide cubes with pyrophyllite gaskets. The resulting cubic assembly was placed into the press. In the following, the sample was pumped up to the final pressure with a rate of 2 GPa/h. After the final pressure was reached, the sample was heated to the final temperature with a heating rate of 100 K/min. The pressure was released with a rate of 3 GPa/h. After normal pressure was reached, the samples were extracted from the octahedron.

Characterization of the Materials:

The formation of the coesite phase, study of its structure and microstructures were carried out by x-ray diffraction (XRD), transmission electron microscopy (TEM), scanning electron microscopy (SEM), and the Raman spectroscopy. The TEM images were taken on a JEOL JEM-2000 electron microscope operated at 200 kV. Samples for the TEM analysis were prepared by dispersing the particles in acetone and dropping a small volume of it onto a holey carbon film on copper grid. Energy dispersive X-ray analysis (EDS) of the sample was carried out using Oxford ISIS EDS with a light element detector. SEM images of the specimen were taken on a Hitachi S-4300 SEM. The XRD pattern were recorded using a Rigaku Rapid II diffractometer with a Mo Kα radiation source (λ = 0.071073 nm). Some samples were measured using Rigaku Rotaflex diffractometer with a Cu Kα radiation source (λ = 0.15405 nm). The Raman spectrum of the specimen was collected using a Horiba-Jobin Yvon LabRam-HR spectrometer equipped with a confocal microscope (Olympus BX-30), a 532-nm notch filter, and a single stage monochromator. The Raman spectrum was collected with 532 nm excitation (20 mW, YAG laser) in the 100–4000 cm^{-1} region. The spectrum was collected at ambient condition. The FT-IR spectra were collected on Thermo Mattson Satellite FT-IR spectrometer, using KBr pellets.

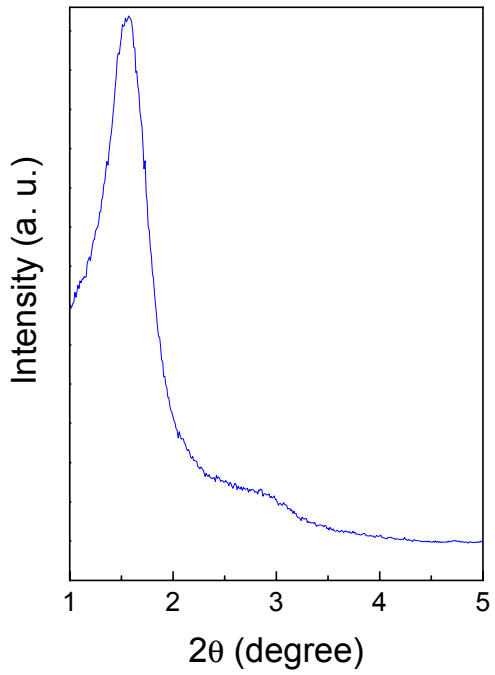

Fig. S1: SAXS pattern of Et-PMO showing periodic order of the mesopores.

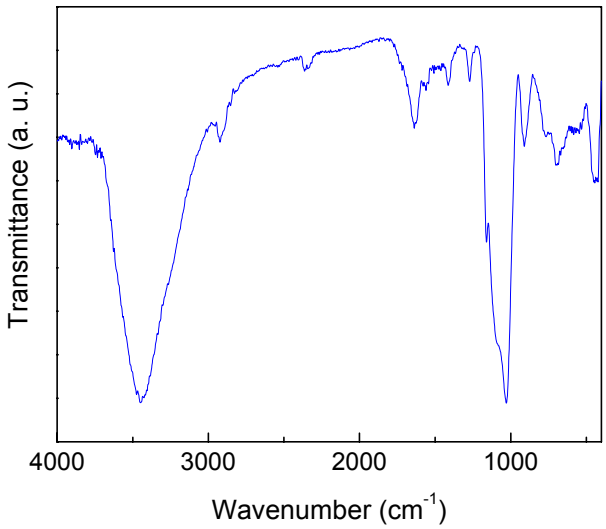

Fig. S2: FT-IR spectrum of as-synthesized Et-PMO showing presence of silanol groups/adsorbed water.

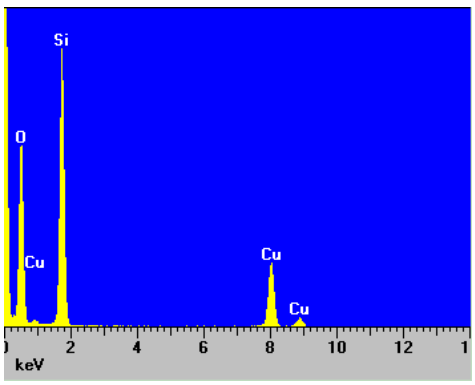

Fig. S3: EDS pattern of Et-PMO heated at 300 C for 150 min at 12 GPa.