

CO₂ as a smart gelator for Pluronic aqueous solution

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1. EXPERIMENTAL PROCEDURES

Materials. F87 (EO₆₂PO₃₉EO₆₂) was provided by BASF company and used without further purification. CO₂ (>99.95% purity) and ethylene (>99.9% purity) were provided by Beijing Analysis Instrument Factory. Double-distilled water was used throughout the experiments. Methyl orange (MO, analytical grade) and hydrochloric acid were provided by Beijing Chemical Plant. Tetraethoxysilane (TEOS, purity ≥ 99%) was provided by Alfa Aesar China (Tianjin) Co., Ltd.

Phase behavior observation. The apparatus for determining the high-pressure phase behavior was similar to that reported previously.¹ It was composed mainly of a high-pressure pump, a constant-temperature water bath, a pressure gauge, a view cell with a magnetic stirrer. In the experiment, the F87 aqueous solution was loaded into the cell and CO₂ was charged into the cell until a suitable pressure was reached at 25 °C. A magnetic stirrer was used to accelerate the mixing of CO₂ and the solution. After the system had reached equilibrium, the stirrer was stopped and the phase behavior was observed.

Small angle X-ray scattering (SAXS). SAXS experiments were carried out at Beamline 1W2A at the Beijing Synchrotron Radiation Facility (BSRF). The data were collected using a Pilatus detector with maximum resolution of 981 × 1043 pixels. The wavelength of X-ray was 1.54 Å, and the distance of the sample to detector was 1.31 m. The high-pressure SAXS cell was the same as that used previously.² In a typical experiment, the suitable amount of 20 wt% F87 aqueous solution was charged into the cell. Then CO₂ was compressed into the cell to the desired pressure. The X-ray scattering data were recorded at 25 °C after equilibrium had been reached. The 2-D

SAXS images were obtained from the detector and then azimuthally averaged to produce one-dimensional profiles of intensity (I) versus wave vector (q) using the two-dimensional data reduction program FIT2D.

UV-vis spectra. The apparatus for determining the high-pressure UV-vis spectra was similar to that reported previously.³ In a typical experiment, the desired amount of 20 wt% F87 aqueous solution that contained MO was added into the high-pressure cell. Then CO₂ was charged into the cell until the desired pressure was reached. A stirrer was used to accelerate the dissolution of CO₂ in solution. The UV-vis spectrum was recorded at 25 °C.

SiO₂ Synthesis. In a typical experiment, 0.5 mL TEOS was added into 5 mL 20 wt% F87 aqueous solution. Then CO₂ was charged into the mixture under magnetic stirring. CO₂ pressure was increased to 4.50 MPa to get the F87-water gel. The gel was stabilized for 12 h at 25 °C to allow complete hydrolysis of the TEOS to form porous SiO₂. After releasing CO₂, the mixture was washed using water and ethanol for several times. Porous SiO₂ were obtained after drying at 60 °C overnight under vacuum.

2. RESULTS

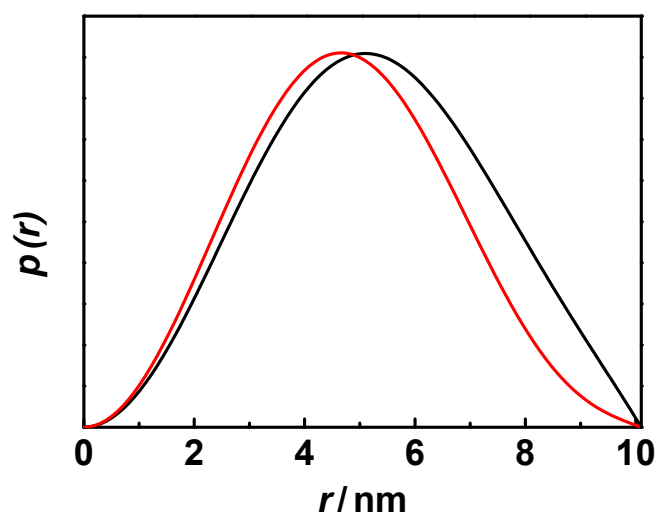


Fig. S1 Normalized pair-distance distribution function curves corresponding to the SAXS patterns of 20 wt% F87 aqueous solution (black) and at CO₂ pressure 2.26 MPa (red).

Table S1. Peak positions for the ordered structures extracted from SAXS measurements.

P /MPa	q^* /nm ⁻¹	$(4/3)^{1/2}q^*$ /nm ⁻¹	$(8/3)^{1/2}q^*$ /nm ⁻¹	$3^{1/2}q^*$ /nm ⁻¹	$(11/3)^{1/2}q^*$ /nm ⁻¹	$2q^*$ /nm ⁻¹
3.80	0.495	/	/	0.862	/	/
4.02	0.497	/	/	0.867	/	0.998
4.10	0.471	/	0.782	/	/	0.925

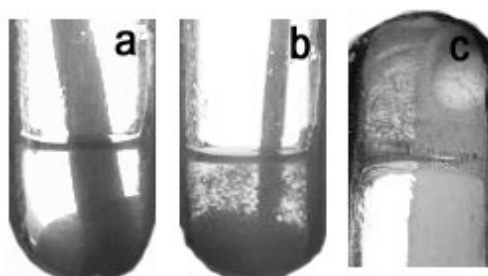


Fig. S2 Photographs of 20 wt% F87 aqueous solution without ethylene (a) and in presence of ethylene at 2.64 MPa (b, c) and 35 °C.

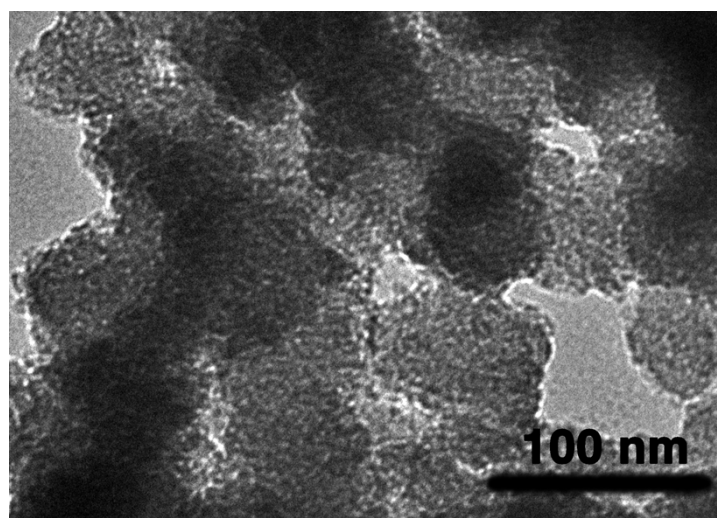


Fig. S3 TEM image of the SiO₂ synthesized in the CO₂-induced gel.

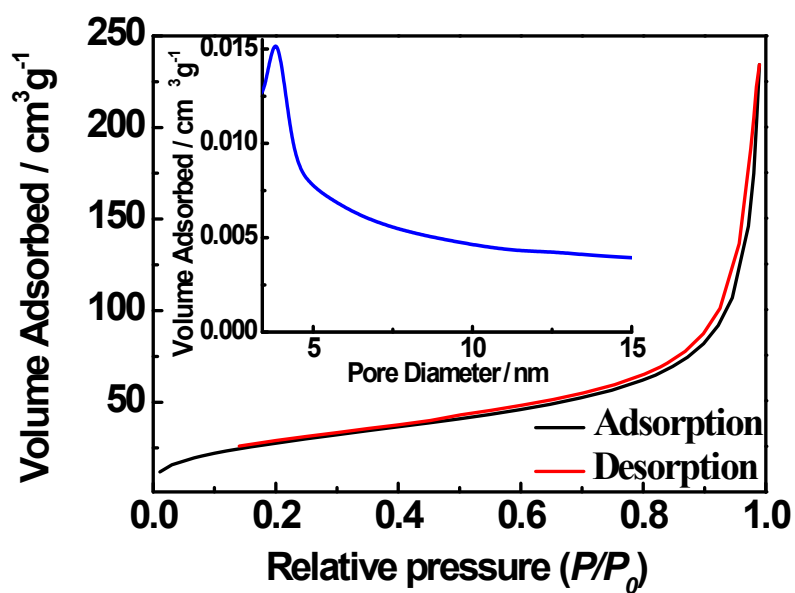


Fig. S4 N₂ adsorption-desorption isotherms of the SiO₂ synthesized in the CO₂-induced gel. The inset shows the mesopore size distribution.

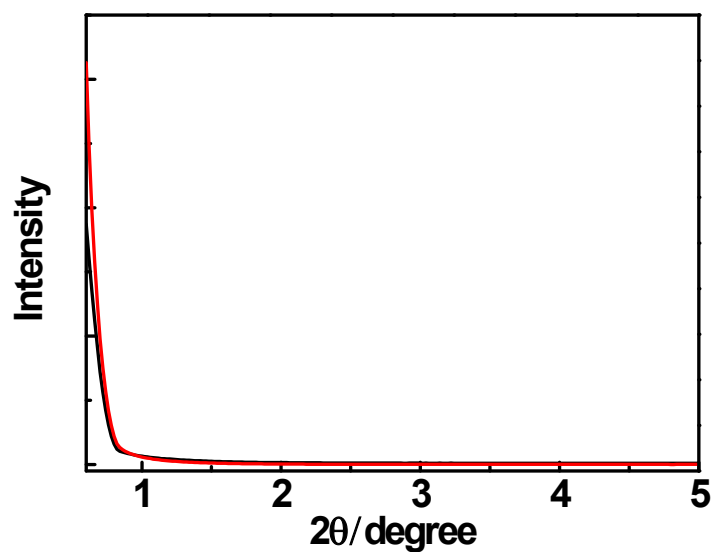


Fig. S5 Small-angle X-ray diffraction patterns of slide blank (black) the SiO₂ synthesized in the CO₂-induced gel (red).

References

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