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# ELECTRONIC SUPPLEMENTARY INFORMATION

# TO

# Bicontinuous Macro-Mesoporous Silica Monoliths obtained by Phase Separation in Non Aqueous Media

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## PREPARATION OF THE DIFFERENT MONOLITHS

### Preparation of silica monoliths from the system TMOS / PEO / FA

Silica monoliths were prepared exploring the system TMOS, PEO 10000 and FA using the molar ratios TMOS / FA / PEO at 2 / 15.6 / y, with y corresponding to different EO/Si ratio between $0.17 < EO/Si < 1.10$. As an example, a bicontinuous monolith with a well-defined macroporosity was obtained with the following molar ratio: $2 / 15.6 / 2.50.10^{-3}$ corresponding to EO/Si = 0.28. First, 0.17 g of PEO 10000 was added in 4 mL of FA and stirred for 30 minutes at room temperature. Then 2 mL of TMOS was added slowly and the solution was stirred gently at room temperature. The resulting transparent solution was poured into a 5 mm internal diameter glass tube of 10 cm length ; it is noteworthy that the surface of glass molds were prior hydrophobized with a 3 %v/v solution of dichlorodimethylsilane ($(CH_3)_2SiCl_2$) in toluene followed by several successive washing in ethanol and toluene; this hydrophobization of the glass tubes avoided any interaction of the monolith with its mold and leaded to a smooth external surface of the silica monolith. Subsequently, the mold was sealed and kept in air at room temperature (22°C) for phase separation and sol-gel transition. The monolithic wet gels were obtained after few minutes (21 min for the ratio EO/Si = 0.28) to 1 h depending on the polymer amount. The gels were then left for aging for 5 days at room temperature (or for 3 days at 40°C). Some shrinkage occured and wet silica monoliths of 4.5 mm diameter monoliths were obtained, released from their glass mold and washed in ethanol for 30 minutes at room temperature.

### Preparation of silica monoliths from the system TMOS / PEO / BMIM-TFSI / FA

Silica monoliths were prepared by adding ionic liquid as second additive to the polymer. Silica monoliths were then synthesized exploring the system TMOS, PEO 10000, BMIM-TFSI and FA using the molar ratios TMOS / FA / PEO / BMIM-TFSI in the range $2 / 15.6 / 2.08.10^{-3}$ (EO/Si = 0.23) / x with $0.125 < x < 2.0$. As an example, a bicontinuous monolith with a well-defined macroporosity was obtained for x = 2. First, 2.84 g BMIM-TFSI was added to 0.07 g PEO in presence of 2 mL FA and stirred gently at room temperature for 30-40 min. Then, 1 mL TMOS wad added slowly and the mixture was stirred for several minutes at room temperature. The resulting transparent solution was poured into a 5 mm internal diameter glass mold. Subsequently, the mold was sealed and kept in air at 40°C for phase separation and sol-gel transition. The monolithic wet gels were obtained after few minutes (25 minutes at RT for x = 2) to 2 h depending on the amount of BMIM-TFSI. The gels were then left for aging for 5 days at room temperature (or for 3 days at 40°C). The same shrinking as previously of the monolithic gel occurred (from 5 to 4.5 mm), and wet monoliths were then released from their glass mold and washed in ethanol for 30 minutes at room temperature.

### Preparation of silica monoliths from the system TMOS / MTMS / FA / PEO / BMIM-TFSI

Silica monoliths were prepared by adding methyltrimethoxysilane (MTMS) together with TMOS to obtain functionalized silica surface. Silica monoliths were then synthesized exploring the system TMOS, MTMS, PEO 10000, BMIM-TFSI and FA using the molar ratios TMOS / MTMS / FA / BMIM-TFSI / PEO in the range $1.75 / 0.25 / 15.6 / x / y$ with $0.1 < EO/Si < 1.5$. As an example, bicontinuous monoliths with a well-defined macroporosity were obtained for x = 0.25, 0.5, 0.7 and $y = 2.08.10^{-3}$ (EO/Si = 0.23). First, 1.98 g BMI-TFSI was added to 0.14 g PEO in presence of 4 mL FA and stirred gently at room temperature for 30-40 min. Then, 1.75 mL TMOS and 0.25 mL MTMS were added slowly and the mixture was stirred for several minutes at room temperature. The resulting transparent solution was poured into a 5 mm internal diameter glass mold. Subsequently, the mold was sealed and kept in air at 40°C for phase separation and sol-gel transition. The gels were then aged for 5 days at room temperature (or for 3 days at 40°C). Wet monoliths were then released from their glass mold and washed in ethanol for 30 minutes at room temperature.

**Figure 4.** Characterization of a dried silica monolith synthesized from the mixture (2 TMOS / 15.6 FA / PEO with EO/Si = 0.28): (A) Mercury porosimetry, (B) Nitrogen sorption isotherm at 77 K, (B) TGA and (D) Nitrogen sorption isotherm at 77 K of monolith with (instead of silanization) an hydrothermal treatment at 125°C for 1 day with 0.1 M $NH_4OH$.

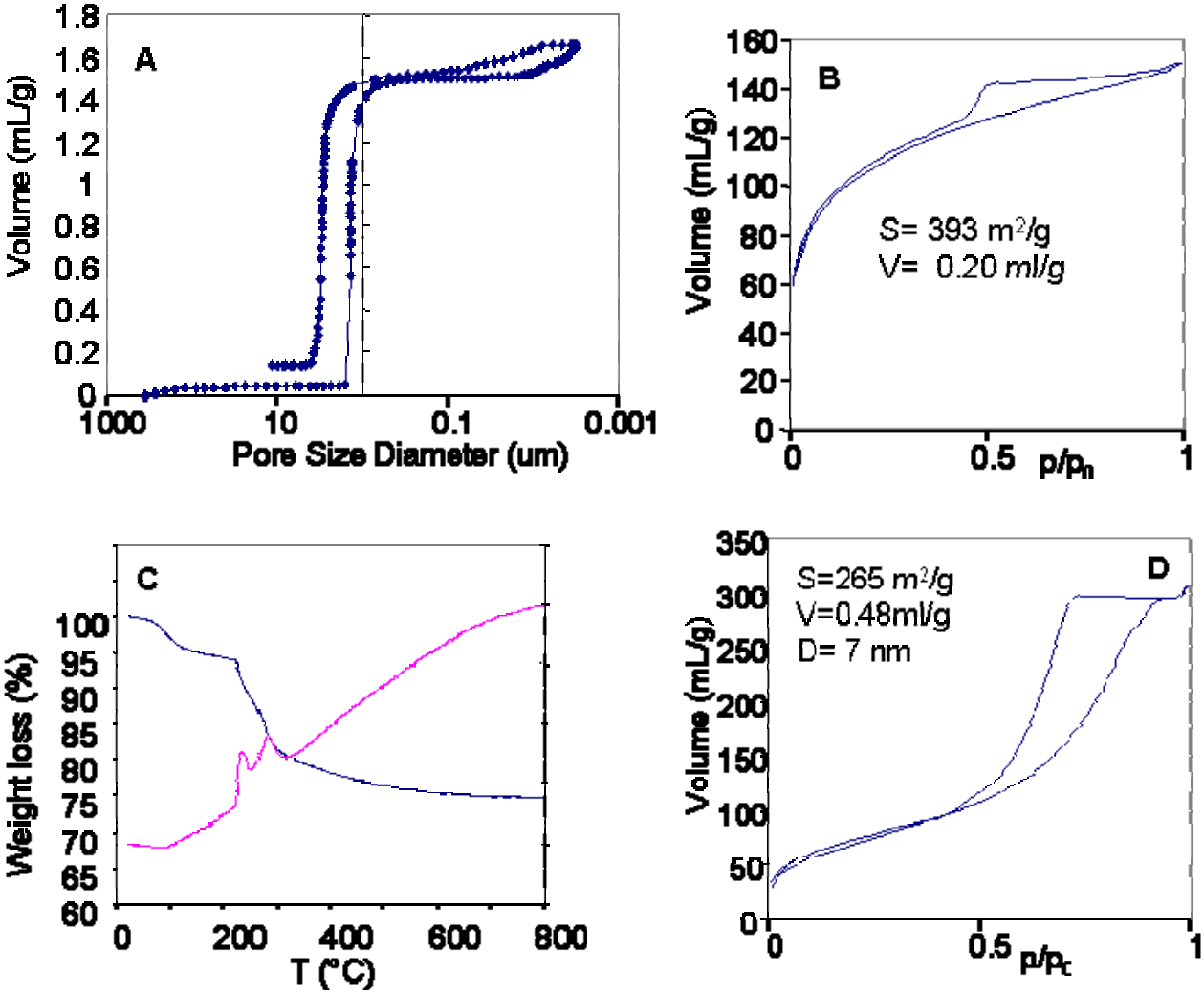

**Figure 5.** Characterization of a dried silica monolith synthesized from the mixture (2 TMOS / 15.6 FA / 2 BMI-TFSI / PEO with EO/Si = 0.23): (A) SEM picture, (B) Nitrogen sorption isotherm at 77 K, (C) Mercury porosimetry, (D) TGA.

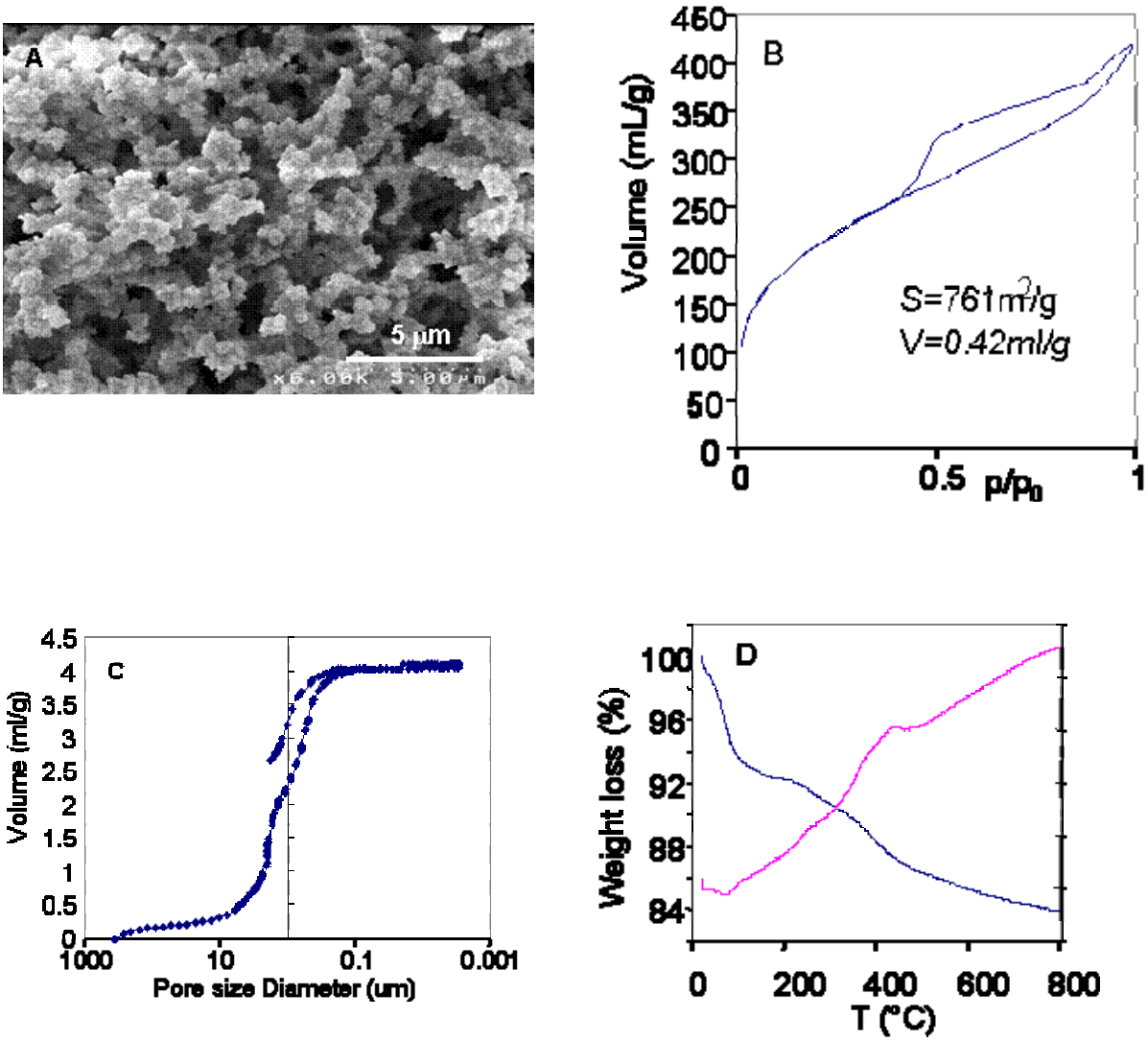

**Figure 6.** Characterization of a dried silica monolith synthesized from the mixture (1.75 TMOS / 0.25 MTMS / 15.6 FA / x BMI-TFSI / PEO with EO/Si = 0.23): (A) SEM picture for x = 0.5 and for x= 0.7 (B) Nitrogen sorption isotherm at 77 K, (C) Mercury porosimetry, (D) TGA.