Impact of the Silica Surface Nanoconfinement on the Microstructure of Alkoxysilane Layers Grafted by Supercritical Carbon Dioxide

Diane Rébiscoul†~, Susan Sananes Israel†, Samuel Tardif‡, Vincent Larrey#, André Ayral§, Francois Rieutord‡

† CEA, ICSM – UMR 5257 CEA-CNRS-UM-ENSCM, 30207 Bagnols-sur-Cèze Cedex, France

‡ Univ. Grenoble Alpes, CEA, IRIG-MEM, F-38000 Grenoble, France

Univ. Grenoble Alpes, CEA, LETI, F-38000 Grenoble, France

§ Institut Européen des Membranes, IEM, UMR-5635, Université de Montpellier, ENSCM, CNRS, Place Eugène Bataillon, 34095 Montpellier cedex 5, France

~Corresponding author: diane.rebiscoul@cea.fr

Table S1. Physicochemical properties of the grafted molecules. Molecule length l_{al} is calculated using ChemSketch software and from[16]. ρ_{eal} is calculated for each molecule as $\rho_{eal} = \rho_m \frac{\sum_i cjZj}{\sum_i cjAj}$, where c_j is the amount of element j in the material, Z_j is the atomic number, A_j is the atomic mass and ρ_m (g.Å^{-3}) is the mass density.

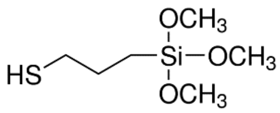
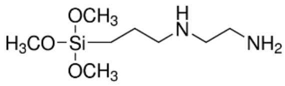
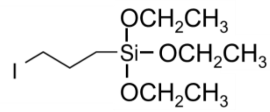
Molecule	MPTMS	AEAPTMS	IPTES
Chemical formula			
ρ_m (g.cm^{-3})	1.01	1.06	1.48
ρ_{eal} (e-.Å^{-3})	0.33	0.34	0.40
l_{al} (Å)	10	12[15]	10

Table S2. Thickness *th* and electron density ρ_e of the layer grafted obtained from the simulation of the X-ray reflectivity curves from [16].

Sample	Molecule	T (ºC)	*th* (Å)	ρe (e-.Å^{-3})	Roughness grafted layer (Å)
MPT-60	MPTMS	60	13.6	0.326	3
AEA-60	AEAPTMS	60	11.1	0.272	8
IPT-100	IPTMS	100	17.8	0.407	2

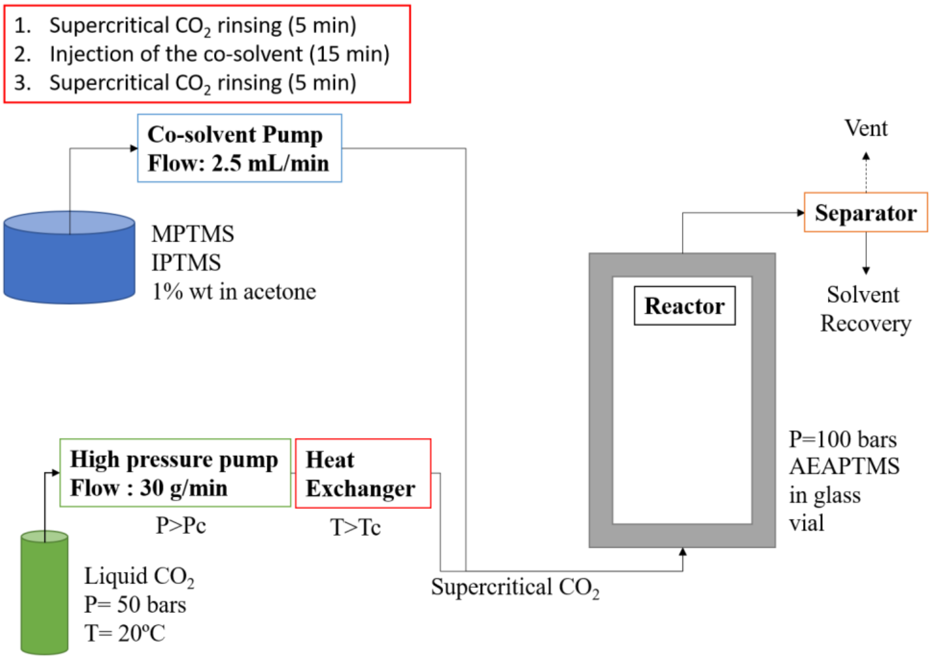


Figure S1: Experimental setup of the SC CO_2 grafting process.

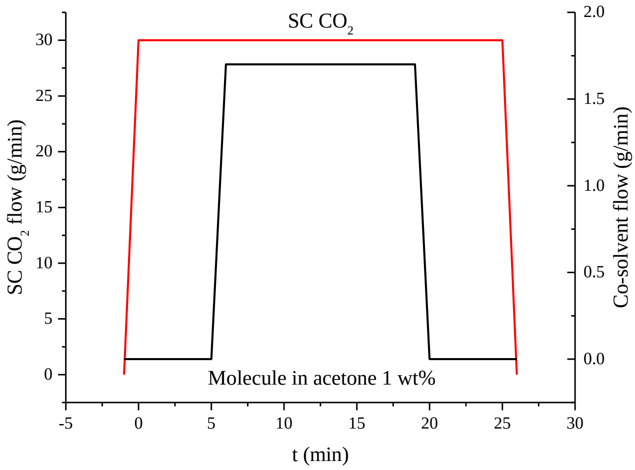


Figure S2. SC CO_2 and solvent flow applied during the SC CO_2 grafting process with MPTMS and IPTMS molecules.

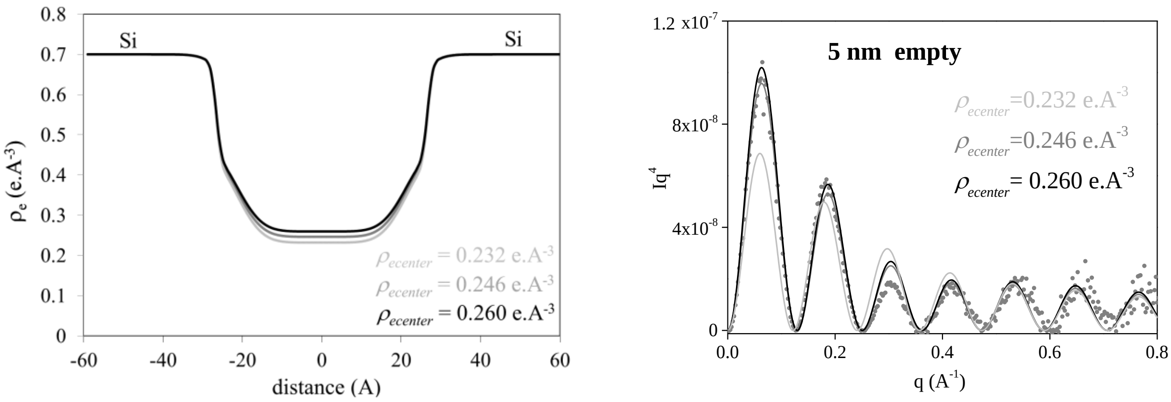


Figure S3. Impact of the variation of the electron density in the center of the nanochannels $\rho_{ecenter}$ of ± 0.014 e.Å^{-3} on X-ray reflectivity curves.

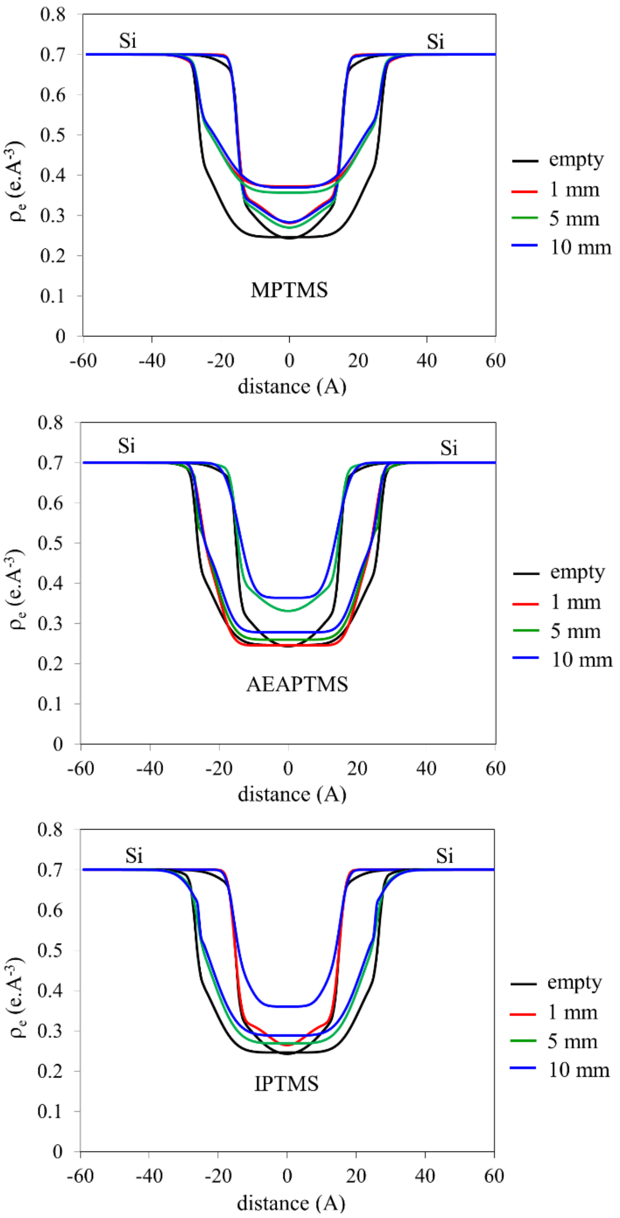


Figure S4: Electron density profiles obtained from the model used for the fitting of the experimental X-ray reflectivity curves of the samples before and after SC CO_2 grafting processes with MPTMS, AEAPTMS and IPTMS at 1, 5 and 10 mm from the entrance of the 3 and 5 nm nanochannels networks.

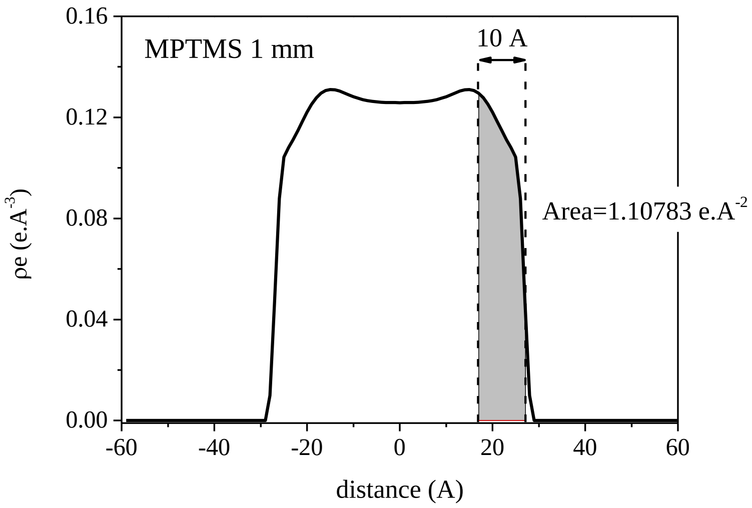


Figure S5: Example of the area determination taking into account the surface density of electron on a distance corresponding to the molecule length for 5 nm nanochannels network grafted with MPTMS at 1 mm from the nanochannels network entrance.

SI1. Origin of the electron density profile: grafted silica surface of Si wafer or/and grafted silica surface of SiO_2 nanochannels

In order to determine if the added electron density in the nanochannels after the SC CO_2 process is mainly due to the alkoxysilanes grafting on the silica surface of Si wafer (top and bottom) and/or on the side silica surface of SiO_2 nanochannels (Figure S6), the two electron densities were calculated supposing a monolayer grafting. The first one is the electron density of a monolayer grafted on the silica of the Si wafer ρ_{ew}. The second one is the electron density of a monolayer on the silica surface of the SiO_2 nanochannels ρ_{en}.

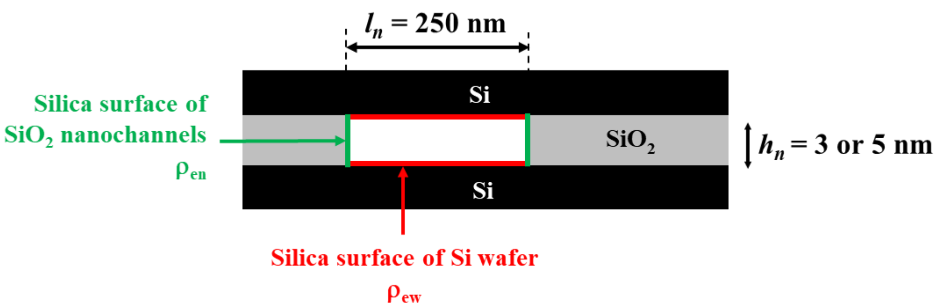


Figure S6: Description of the parameters used to calculate the electron density of a monolayer on the various silica surface of the nanochannels.

Thus, considering that the accessible surface of silica on Si wafer contributes to 50 % of the total surface in the nanochannels (50% of the Si wafer is covered by the SiO_2 nanochannels), the electron density of a monolayer grafted on the silica of the Si wafer can be written as $\rho_{ew}(1)$:

$$\rho_{ew} = \rho_{eal}/2 \tag{1}$$

With ρ_{eal} (e.Å^{-3}), the electron density of the liquid alkoxysilane (Table S1) or the density of the grafted layer measured in [16].

The electron density of a grafted layer on the silica surface of the SiO_2 nanochannels can be calculated from the number of electrons in the grafted monolayer n_{en} (2):

$n_{en} = 2\rho_{eal}.l_{al}.L.h_n$

(2)

with l_{al} (Å) the thickness of the grafted layer, L (Å) the sample length and h_n (Å) the height of the nanochannels.

Considering the volume of a nanochannel v (Å^3) (3):

$v = l_n L.h_n$

(3)

With l_n (Å) the width of one nanochannels and taking into account that SiO_2 nanochannels contribute to 50 % of the total volume of the nanochannels, the electron density of a grafted layer on the silica surface ρ_{en} (e.Å^{-3}) of the nanochannels can be written as (4):

$\rho_{en} = \frac{\rho_{eal}.l_{al}}{l_n}$

(4)

These values were calculated following two approaches. First, ρ_{ew} and ρ_{en} were determined considering the grafted layer thickness as the molecule length and the mass density of the liquid alkoxysilane ρ_{eal} (e.A^{-3}) (Table S1). Second, $\rho_{ew}*$ and $\rho_{en}*$ were calculated from the thickness and the density obtained by X-ray reflectivity for a layer grafted on a large flat surface[16]. The obtained values are presented in the Table S3.

Table S3 : Electron densities of a monolayer grafted on the silica of the Si wafer ρ_{ew} and electron density of a monolayer on the silica surface of the SiO_2 nanochannels ρ_{en}. ρ_{ew} and ρ_{en} were calculated from Tablea SI and ρ_{ew}* and ρ_{en}* were calculated from [16].

	ρ_{ew} (e.A^{-3})	$\rho_{ew}*$ (e.A^{-3})	ρ_{en} (e.A^{-3})	$\rho_{en}*$ (e.A^{-3})
MPTMS	0.166	0.163	0.001	0.002
AEAPTMS	0.170	0.136	0.003	0.001
IPTES	0.201	0.142	0.002	0.002

As presented in Table S3, the ρ_{en} values are negligible regarding ρ_{ew}, and represent at a maximum 2 % of the $\Delta\rho_e$ shown in Figure 5. This is not surprising considering the high aspect ratio of the channels (3-5 nm high, 250 nm wide). Consequently, the added electron densities in the nanochannels presented in Figure 5 are mainly due to the alkoxysilanes grafted at the silica surface of the Si wafer.