## Controlled Photo-Oxidation of Nanoporous Polymers

by:





**S1**. Illustration of the significant difference between sensitivity of photo-oxidation for a nanoporous material (NP) and a 'conventional' non-porous material, both of polystyrene (not cross-linked). One Polystyrene-*b*-PDMS polymer of total molecular mass 140 kg/mol of which 29% is silicone (hexagonal morphology), was prepared by living anionic polymerization in THF. Then samples of between 0.5 and 1 g of polymer were solvent cast onto flat bottom Petri dishes from 10% (w/w) THF solutions. THF was left to evaporate for 48 h under a gentle stream of Argon. The 0.15 - 0.30 mm thick films obtained were then treated with hydrogen fluoride, HF, to obtain the NP PS (**Caution: HF is hazardous, must be handled with due precautions!**). The procedure of preparation of nanoporous polystyrene can be found in: Ndoni, S.; Vigild, M. E.; Berg, R. H. *J. Am. Chem. Soc.* **2003**, *125*, 13366.

Due to the high surface area concentration, monitoring of the reaction changes is much more sensitive in the case of NP. The figure illustrates the working of the scheme on another polymer than PB, therefore supporting the generality of the procedure mentioned in the main manuscript. The nanoporous PS sample was more opaque than the PB sample of the main manuscript and the observed photo-oxidation depth was about 20  $\mu$ m. Attenuated total reflection (ATR-FT-IR) spectra of nanoporous (a) and non-porous polystyrene (b), before and after 48 h of UV-310 nm treatment under a Philips TL 20W/ 12 RS SLV lamp (CAUTION! This region of UV is particularly hazardous). The radiation intensity at the sample position was estimated to ~7 mW cm<sup>-2</sup>. The red and the orange lines show identical spectra for the NP\_PS and the PS. The green arrows label the wavenumber ranges where most significant changes happen due to UV radiation: the hydroxyl (–OH), the carbonyl (>C=O) and C-O- groups at around 3400 cm<sup>-1</sup>, 1700 cm<sup>-1</sup> and 1000 cm<sup>-1</sup>, respectively. Due to enhanced surface area the changes are significantly larger in the case of NP-PS in (a) than PS in (b). The (area or height) ratio between corresponding absorption peaks in (a) and (b) is expected to correlate with the ratio between the surface areas at the probing depth of ATR-FTIR in the two cases (~ 1  $\mu$ m). Qualitatively the development of absorption bands in (a) is similar to the case of nanoporous polybutadiene.



**S2.** Transmission UV-Vis spectrum  $T(\lambda)$  of nanoporous PB sample before UV treatment and relative power emission spectrum  $I_{rad}(\lambda)$ of the Philips Cleo 25W RS UV lamps used for the irradiation of the nanoporous samples. Radiation fluxes of  $\Phi_{rad} = 31 \pm 2$  mW cm<sup>-2</sup> were measured at the samples' spots in the wavelength range 310-400 nm. The area in red is proportional to the radiation absorbed by the sample at the start of the UV treatment, used for the calculation of the Oxygen fixation quantum yield. The red contour  $I_{abs}(\lambda)$  at t =0 was drawn graphically by the relation  $I_{abs}(\lambda) = I_{rad}(\lambda) [1 - T(\lambda)]$ . This was converted into power absorption flux  $\Phi_{abs}(\lambda)$  and ultimately, again graphically, into photon number absorption rate  $dN_{hv,abs}/dt$  at t = 0 used in the calculation of the quantum yield  $\overline{Q}_{0}^{0}$ .



**S3.** Water mass uptake relative to the UV sample absorbance at 350 nm. The transition for the samples irradiated at 32°C is sharper than for the samples irradiated at 42°C. The error bars are standard deviations calculated from three datasets.





**S4.** (a) UV mediated hydrophilic patterning at 5  $\mu$ m (5  $\mu$ m stripes alternating hydrophilic-hydrophobic) and (b) 20  $\mu$ m (20 x 20  $\mu$ m<sup>2</sup> hydrophilic squares surrounded by 20  $\mu$ m wide hydrophobic corridors).



**S5.** TEM of NP templated Copper; due to long contact with air the original metal in the nano-cavities is expected to be oxidized. The inset shows part of a 'monolayer' gyroid with cavities filled with metal oxide. The darker zones are at the strut positions with largest projected metal thickness (corresponding to the lightest zones in the TEM micrographs of the 'empty' NP shown in manuscript's fig. 2). The large picture shows a high resolution TEM of the inset's first quadrant. The light regions represent the polymer zones. The crystalline structure visible within the gyroid channels is consistent with deformed cuprite, Cu<sub>2</sub>O observed Copper nano-particles in after oxidation (ref. 23 in the manuscript). The filled channels' diameter is measured to  $12 \pm 2$  nm.



**S6.** Zoom of the central part from the previous figure; the inset shows the Fast Fourier Transform (FFT) of crystalline structure consistent with the cuprite (Copper (I) oxide) structure from ref. 23 in the manuscript. The scale-bar in the inset is the *q*-scale, related to real space scale *d* by  $q \cdot d = 2\pi$ . In order of decreasing FFT spot intensity the characteristic lengths/nm in the figure are: 0.248 ( $d_{111}$ ), 0.250 ( $d_{\wedge 111}$ ), 0.311 ( $d_{110}$ ), 0.433 ( $2d_{002}$ ) and 0.217 ( $d_{002}$ ).