

Amine-Modified Silica Nanotubes and Nanospheres: Synthesis and CO₂ Sorption Properties

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S1. Characterization

The procedures used for characterization of unmodified and aminopropyl-modified SNT and SNS are similar to those reported in previous works [1,2]. Nitrogen adsorption isotherms were measured at -196 °C on an ASAP 2010 volumetric analyzer (Micromeritics, Inc., Norcross, GA). Prior to adsorption measurements all samples were out gassed under vacuum at 110 °C for 2 h. Transmission electron microscopy (TEM) images were acquired on a FEI Technai Spirit TEM operated at 120 kV. Before imaging, samples were dispersed in ethanol under sonication and deposited on a carbon-coated copper grid. High resolution thermogravimetric measurements were recorded on TGA Q-500 analyzer (TA Instruments, Inc., New Castle, DE). Thermogravimetric (TG) profiles were recorded from 25 to 780 °C in flowing nitrogen with a heating rate of 10 °C / min using a high resolution mode. The weight of each analyzed sample was typically in 5-20 mg range. The TG profiles were used to obtain information about the extent of the template removal.

¹H-¹³C cross polarization (CP) MAS NMR spectra were recorded using Bruker Avance (III) 400WB NMR spectrometer (Bruker Biospin Corporation, Billerica, MA, USA) with MAS triple resonance probe head using zirconia rotors 4 mm in diameter. ¹H-¹³C CP-MAS NMR spectra were acquired at 400.13 MHz for ¹H and 100.63 MHz for ¹³C. The MAS rate was 5 KHz. ¹H $\pi/2$ pulse length was 3.5 μ s and pulse delay 2.0 s. TPPM20 ¹H decoupling sequence was used during acquisition. The ¹³C chemical shifts were referenced to p-dioxane 66.6 ppm.

S2. Room temperature CO₂ adsorption measurements

Similarly as in [1,2], CO₂ adsorption isotherms were measured on the selected unmodified and aminopropyl-modified SNT and SNS samples in the pressure range up to 1.2 atm using ASAP 2020 volumetric adsorption analyzer (Micromeritics, Inc., GA) at 25 °C and ultrahigh purity (99.99 %) gaseous CO₂. Prior to adsorption analysis each sample was outgassed at 110 °C for 2 h under vacuum.

S3. CO₂ chemisorption and TPD measurements

Similarly as in [1,2], CO₂ chemisorption and TPD experiments were conducted using a Micromeritics Auto Chem II Chemisorption Analyzer (Micromeritics, Inc., GA) equipped with a thermocouple detector (TCD). Approximately 10-100 mg of each sample were loaded in a quartz tube microreactor supported by quartz wool and subjected to pretreatment at 320 °C for 10 min before CO₂ sorption, using a heating rate of 10 °C/min in flowing helium (at a rate of 50 cm³/min). Next, the sample was cooled down to the specified temperature (120 °C) using heating rate of 10 °C/min, exposed to pulse of 5 % CO₂-He (50

cm³/min) as a loop gas, kept for 3 minutes and allowed for return to the baseline. Recording was repeated until peaks are equal or 30 times. Recording was taken every 0.1 seconds and finally post CO₂ pulse purge was applied in flowing helium (50 cm³/min) for 30 min. In the TPD experiments, the samples were heated up to 320 °C using a heating rate of 5 °C/min and kept at this temperature for 90 min. The amounts of desorbed CO₂ were obtained by integration of the desorption profiles and referenced to the TCD signals calibrated for known volumes of analyzed gases. Note that due to some limitations of the available instrument the CO₂ sorption was measured on a volumetric adsorption analyzer (see section S2) instead of the above mentioned chemisorption analyzer.

S4. Calculations

The Brunauer-Emmett-Teller specific surface areas (S_{BET}) were calculated from the N₂ adsorption isotherms in the relative pressure range of 0.05-0.2 using a cross sectional area of 0.162 nm² per nitrogen molecule. The single-point pore volume (V_{sp}) was estimated from the amount adsorbed at a relative pressure (p/p^0) of ~ 0.98. The pore width (W_{max}) was obtained at the maximum of the pore size distribution (PSD) curve obtained by the KJS method [3].

S5. Additional discussion of amine-modified silica nanospheres

While the incorporation of aminopropyl groups through the post-synthesis grafting of silica nanotubes tended to result in the pore size decrease, a less regular trend was observed for the silica nanospheres prepared by co-condensation of aminopropyltriethoxysilane and tetraethylorthosilicate (see Table 1). Specifically, the introduction of the organosilica precursor led to an increased pore diameter, while the further increase in its loading resulted in the pore size decrease. In the absence of a swelling agent, the surfactant-micelle-templated co-condensation process typically results in a decrease in the pore diameter (and often also in the unit-cell size) as the loading of the organosilica precursor decreases [4]. However, in the case studied, the swelling agent was present. The combination of an organosilica precursor (such as aminopropyltriethoxysilane used herein) with the silica precursor (such as tetraethylorthosilicate used herein) may influence the uptake of the swelling agent by the micelles and/or the aggregation number of the surfactant in the micelles, which may impact the pore diameter, and lead to a complicated dependence of the pore size on the organic group loading. For instance, in the case of FDU-12 silica with face-centered cubic structure synthesized using Pluronic F127 in the presence of trimethylbenzene as a swelling agent [5], the combination of trimethylvinylsilane with tetraethylorthosilicate in the gradually increasing proportion led to the unit-cell size and pore size decrease followed by an increase beyond values for pure-silica FDU-12. Further studies would be needed to better understand such behavior.

References

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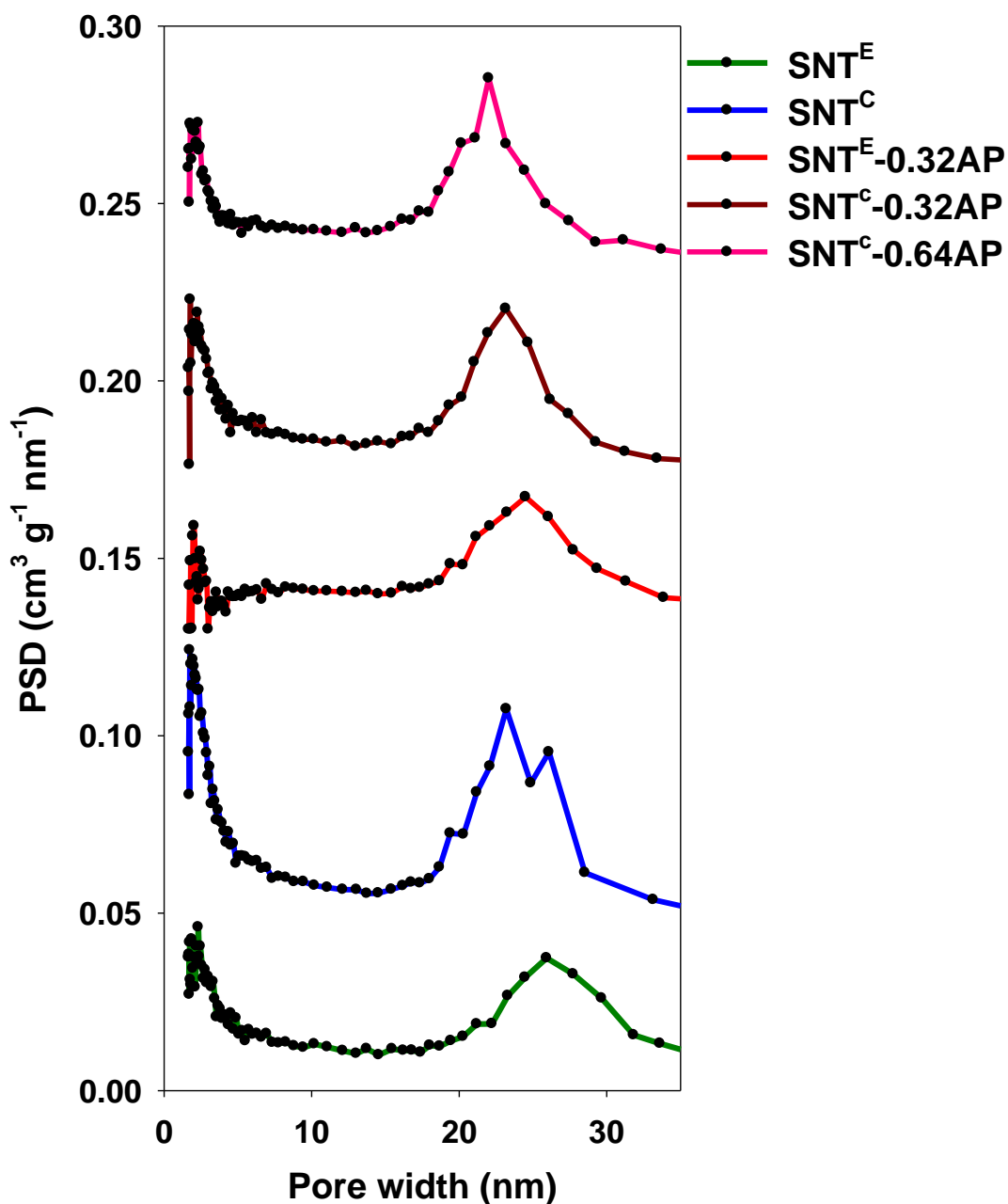


Figure S1. PSD curves for unmodified and aminopropyl-modified SNT samples; the PSD curves 2, 3, 4, and 5 are shifted by 0.09, 0.13, 0.17, and 0.23 $\text{cm}^3 \text{g}^{-1} \text{nm}^{-1}$, respectively, in relation to curve 1. The pore size distributions (PSD) were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by the KJS method calibrated for cylindrical pores (Kruk, M.; Jaroniec, M.; Sayari, A. Application of Large Pore MCM-41 Molecular Sieves to Improve Pore Size Analysis Using Nitrogen Adsorption Measurements. *Langmuir*. **1997**, 13, 6267-6273).

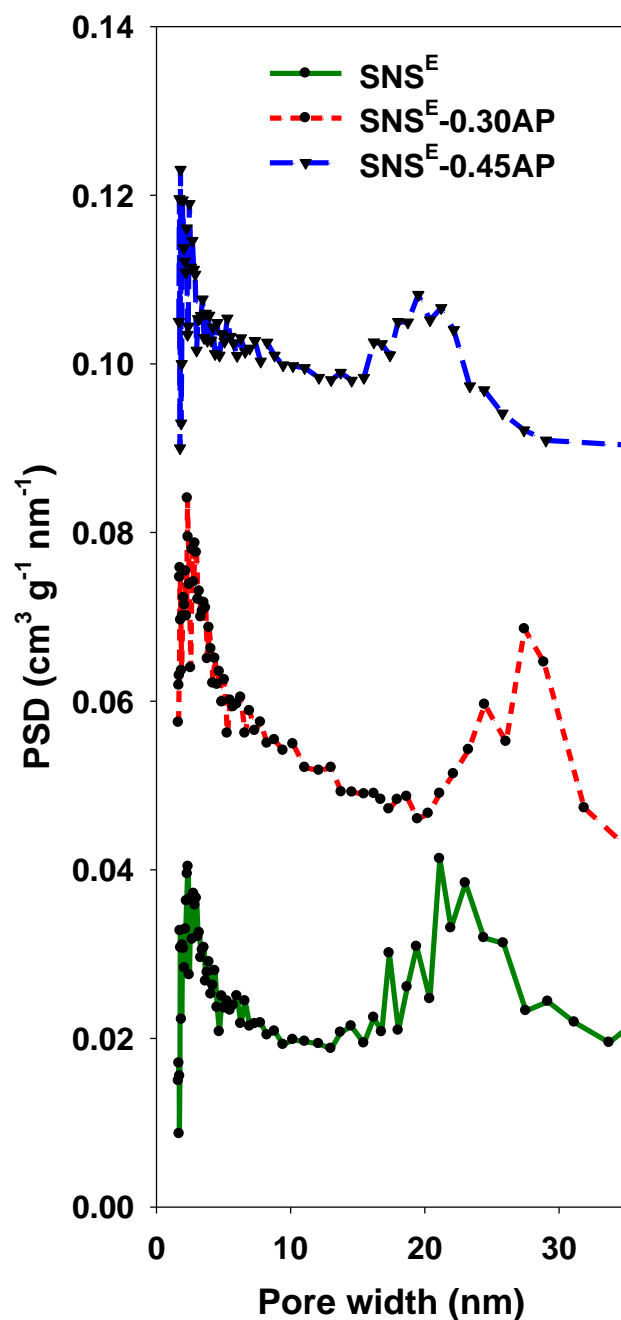


Figure S2. PSD curves for unmodified and aminopropyl-modified SNS samples; the PSD curves 2 and 3 are shifted by 0.05 and 0.09 $\text{cm}^3 \text{g}^{-1} \text{nm}^{-1}$, respectively, in relation to curve 1. The pore size distributions (PSD) were calculated using adsorption branches of nitrogen adsorption-desorption isotherms by the KJS method calibrated for cylindrical pores (Kruk, M.; Jaroniec, M.; Sayari, A. Application of Large Pore MCM-41 Molecular Sieves to Improve Pore Size Analysis Using Nitrogen Adsorption Measurements. *Langmuir*. **1997**, 13, 6267-6273).