Electronic Supplementary Information

Quantification of surface functional groups on silica nanoparticles: comparison of thermogravimetric analysis and NMR

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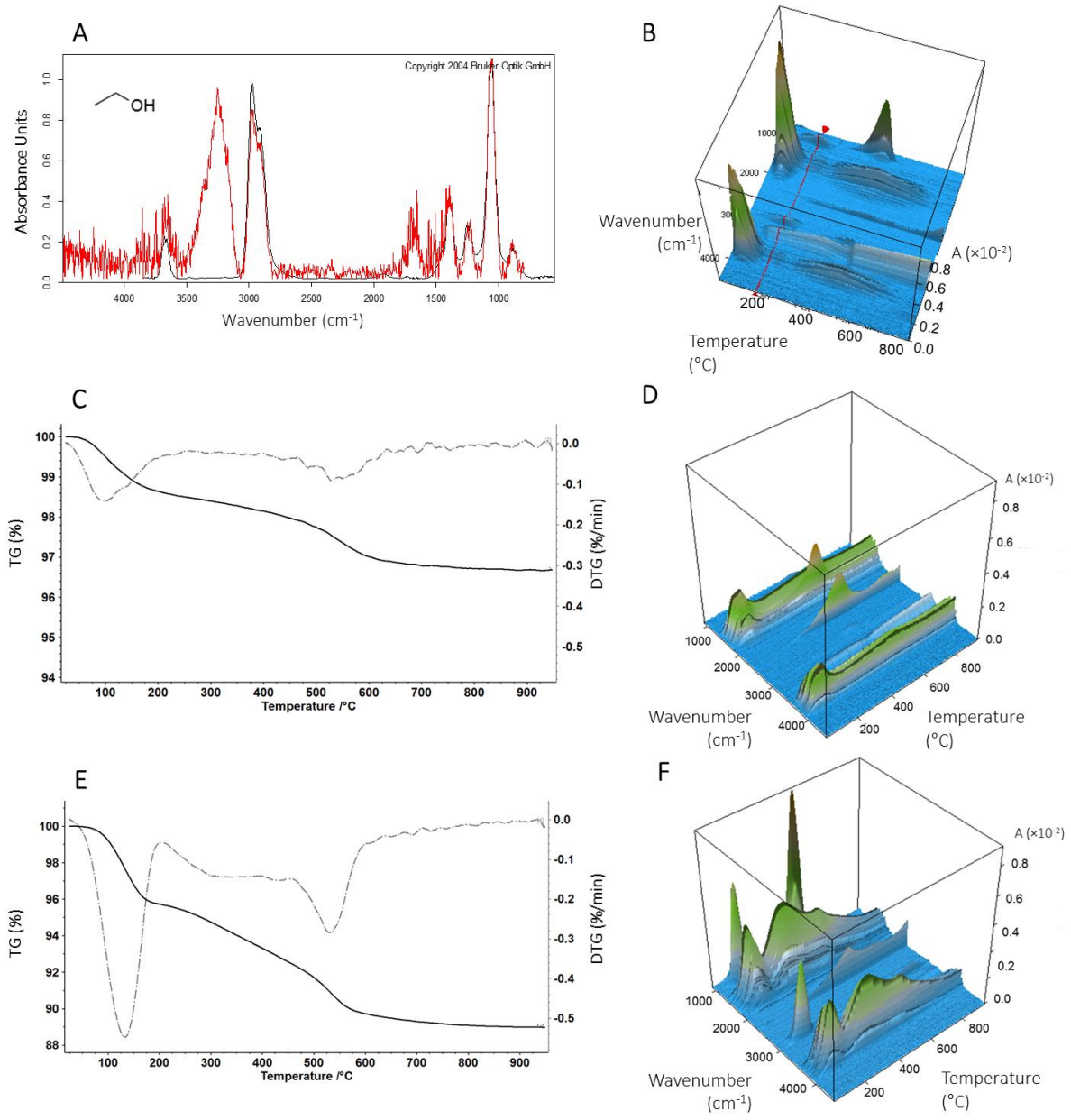

Fig. S1 (A) FT-IR spectrum from EGA of 100 nm bare silica NPs (Supplier A) acquired at 185 °C (red) overlaid with library FT-IR spectrum of ethanol (black); the significant band 3000-3500 cm^{-1} is typically not observed and in this case it is probably an artefact originating from baseline distortion. (B) 3D EGA-FT-IR of the same NPs displayed at a different angle (compared to Fig 1D) to reveal bands corresponding to ethanol with maximum temperature at 185 °C (red line). (C) thermogram of 20 nm bare Stöber silica (Supplier A) and the corresponding EGA-FT-IR spectra (D). (E) thermogram of 200 nm bare Stöber silica NPs (Supplier A) and the corresponding EGA-FT-IR spectra (F).

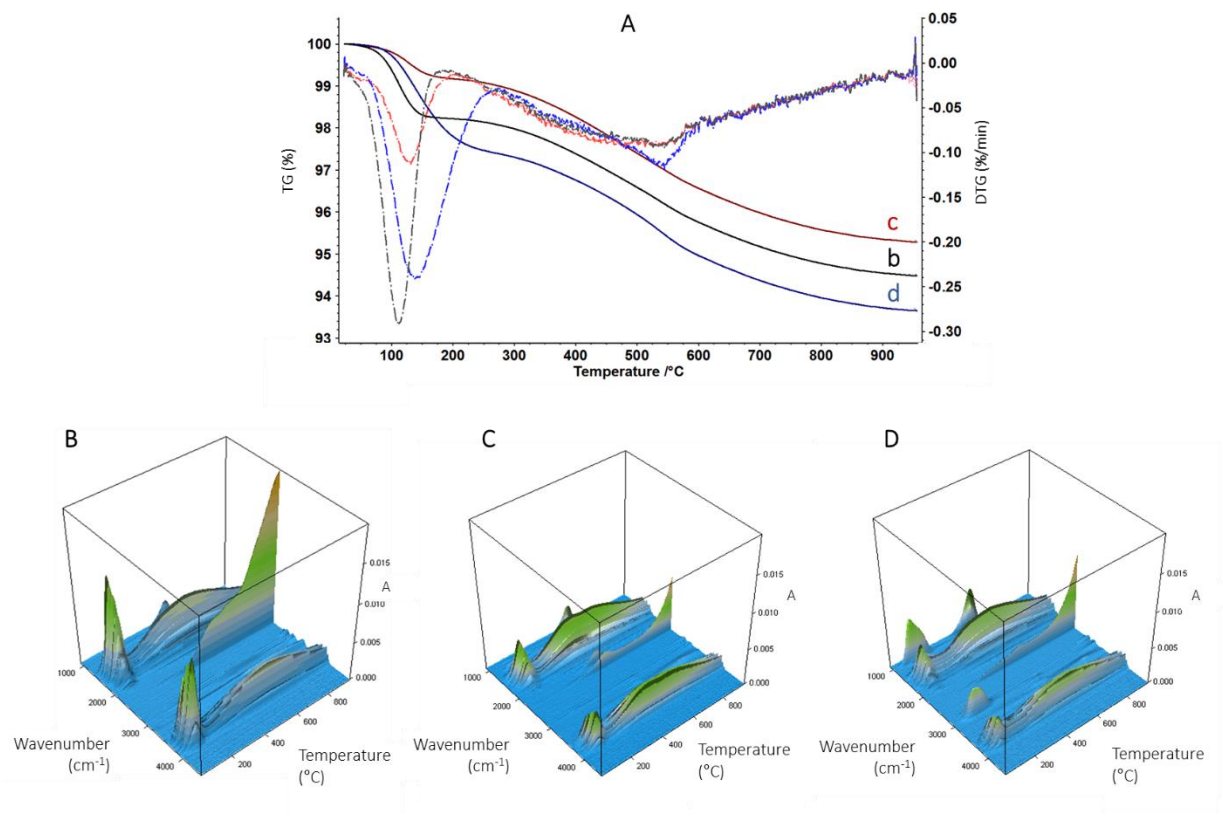

Fig. S2 (A) Thermograms of 100 nm bare silica NPs (Supplier A) analyzed: (b) as received dry powder (1.7 % mass loss <200 °C), (c) after freeze-drying overnight (0.8 % mass loss <200 °C) and, (d) after dispersion in ethanol followed by centrifugation, re-dispersion in water and subsequent freeze-drying (2.6 % mass loss <200 °C). EGA-FT-IR spectra for b, c, and d thermograms are shown in B, C, and D, respectively. The mass loss at > 200 °C is 3.6 %, 3.7 % and 3.8 % for thermograms b, c and d, respectively, indicating that drying or exposure to ethanol followed by drying does not affect the mass loss at higher temperatures.

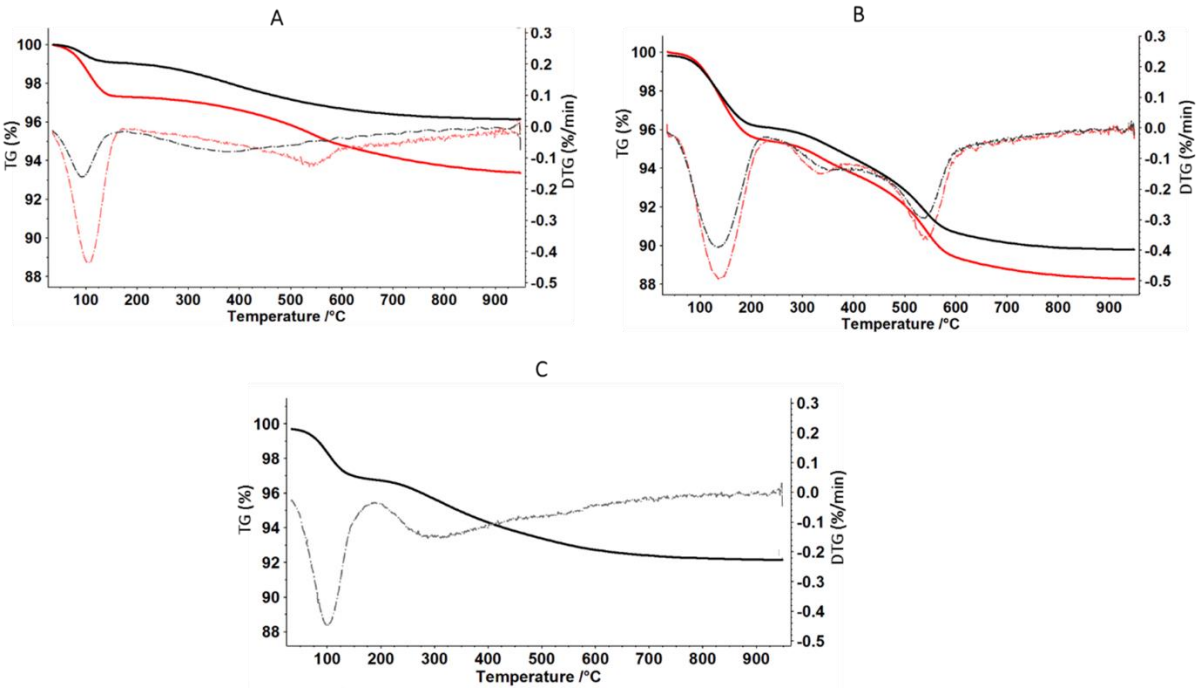

Fig. S3 Thermograms of bare Stöber silica NPs from various sources: (A) Supplier A: 50 nm (red) and 100 nm (black); (B) Supplier B: 50 nm (red) and 100 nm (black); (C) In-house prepared silica 108 nm (DLS z-average, water, 0.1 mg/mL).

Table S1 Repeatability of mass loss observed for non-functionalized Stöber silica at low temperature (<200 °C) and high temperature (> 200 °C).

Sample, n[a]	Mass loss (%) <200 °C	Mass loss (%) >200 °C	Sample history
A 100 nm, n=2	1.1± 0.1	3.7 ± 0.2	Dry powder as received
A 100 nm, n = 3	1.7 ± 0.1	3.5 ± 0.1	Received dry, vacuum dried
A 80 nm, n = 2	0.69 ± 0.2	3.25 ± 0.02	Water, freeze dried
B 200 nm, n = 3	4.4 ± 0.4	6.8 ± 0.2	Dry powder as received

[a] Sample is listed as supplier and size; n is the number of replicate experiments.

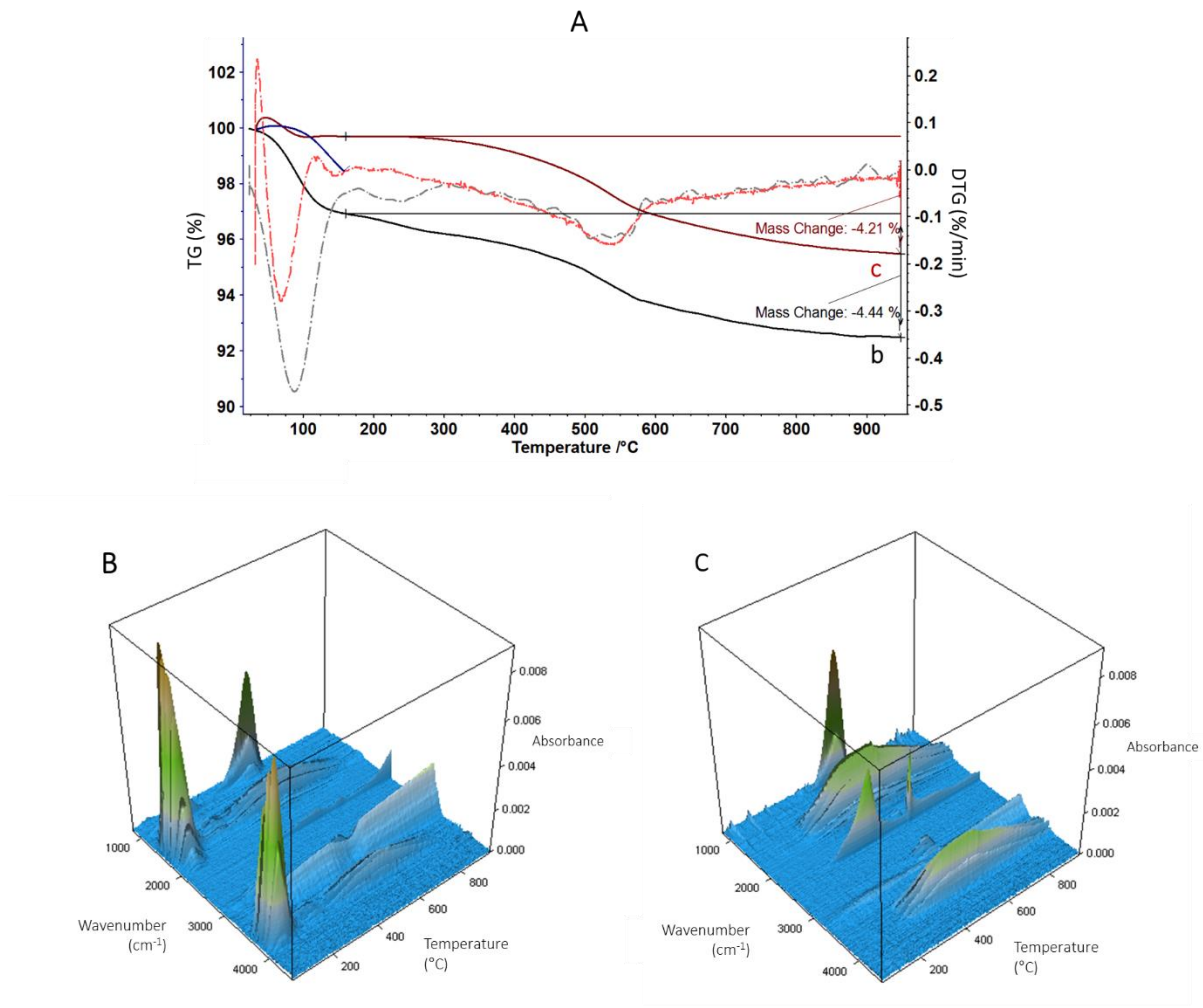

Fig. S4 (A) Thermograms of 100 nm porous silica NPs (Supplier A) analyzed as received (black) and after drying (red); (B) EGA-FT-IR of sample analyzed as received; (C) EGA-FT-IR of the sample dried inside the TGA by an isothermal step at 160 °C for 16 hrs under argon atmosphere and cooled under argon before restarting the thermal cycle.

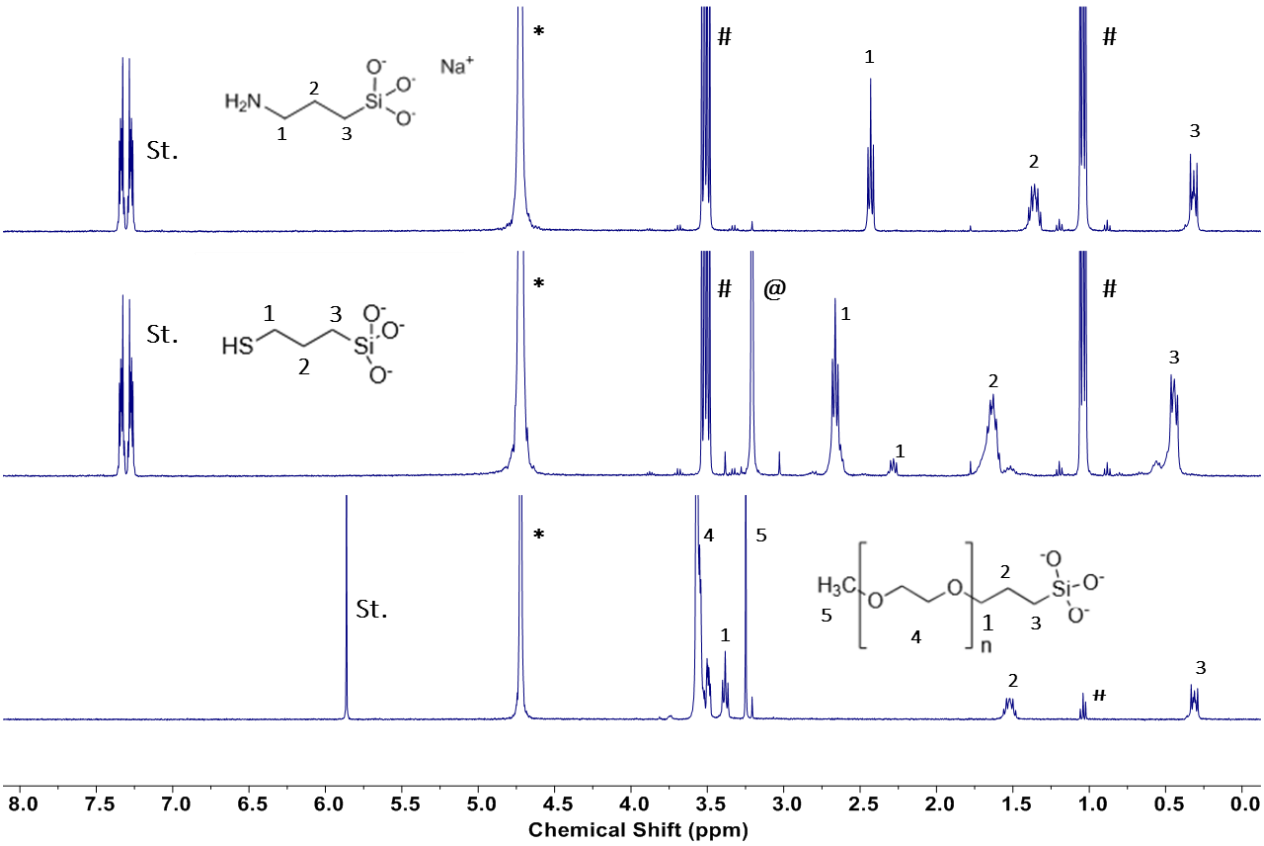

Fig. S5 ^{1}H qNMR spectra of functionalized silica NPs dissolved in 0.4 M NaOD and combined with internal standard 'St.' (potassium hydrogen phthalate or maleic acid). Residual water, ethanol and methanol are denoted by '*', '#', and '@' respectively.

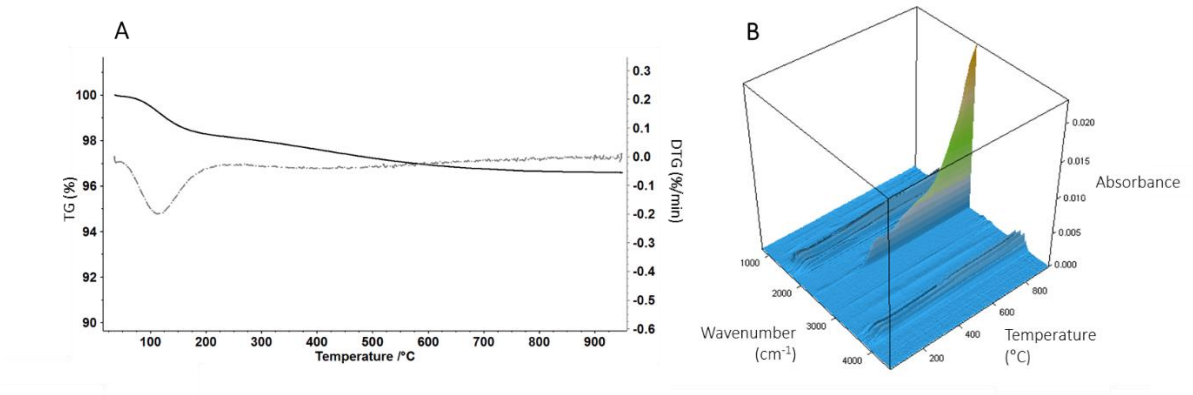

Fig. S6 (A) Thermogram and (B) corresponding EGA-FT-IR of 30 nm bare silica NPs (Supplier C).

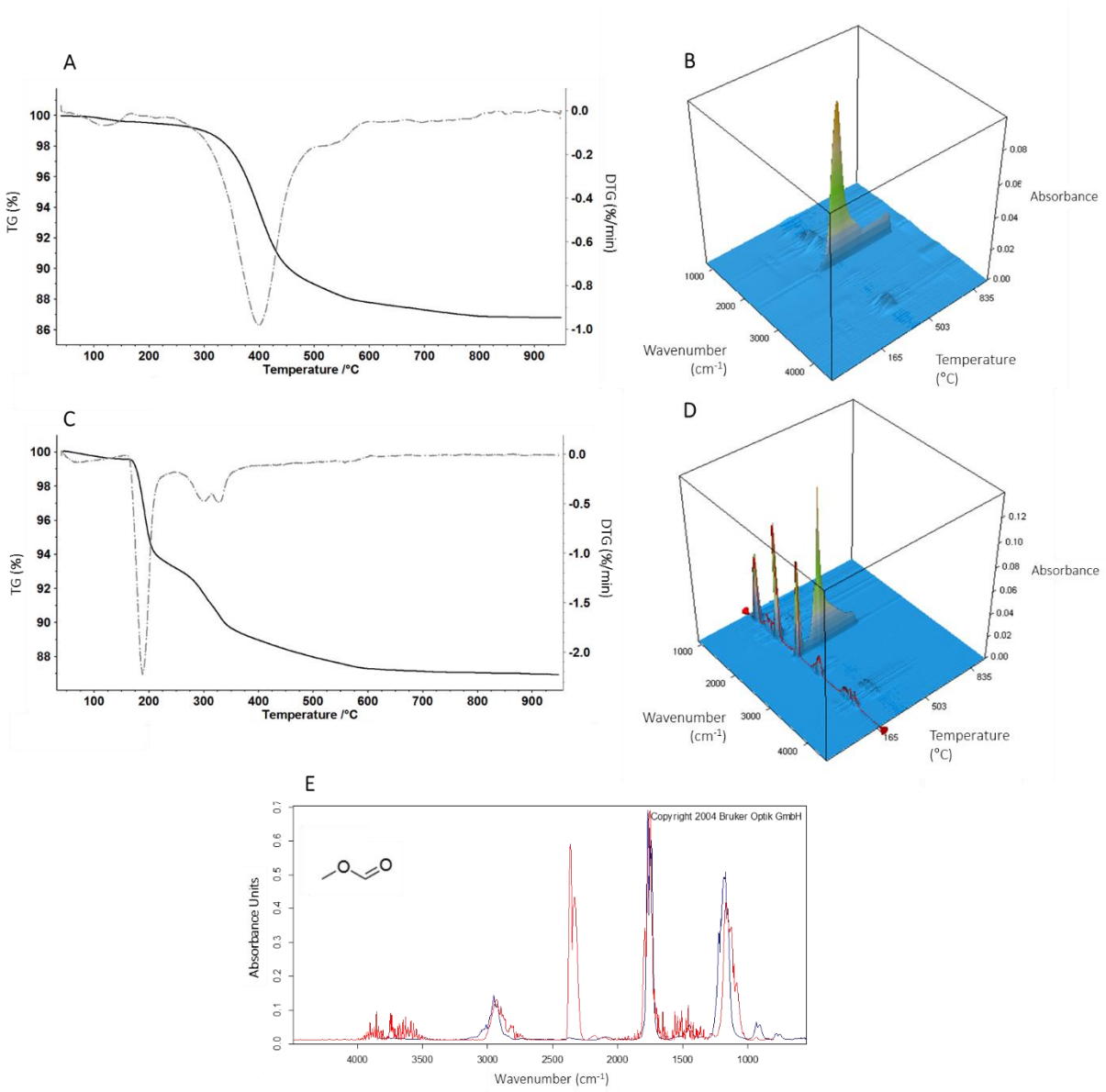

Fig. S7 (A) Thermogram of 30 nm PEG functionalized silica (Supplier C) analyzed in an argon atmosphere with corresponding EGA-FT-IR (B); (C) thermogram of the same sample analyzed in an air atmosphere with corresponding EGA-FT-IR (D); (E) FT-IR spectrum from EGA of the sample analyzed in air acquired at 188 °C (red) and overlaid with the library FT-IR spectrum of methyl formate (blue). The inexact match between spectra suggests that similar semi-oxidized products may be initially formed before the functional group is combusted to CO_2 at higher temperatures. Importantly, the total mass loss observed in argon atmosphere (13.19 %) is almost identical to the total mass loss in air (13.07 %).

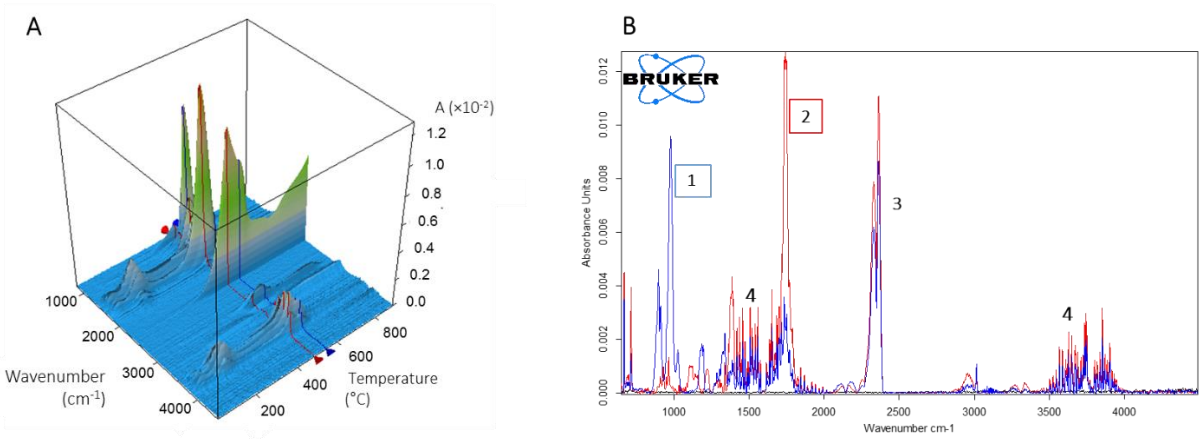

Fig. S8 (A) EGA-FT-IR plot of 37 nm succinate modifed silica NPs. Note that CO_2 is still being released above 750 °C although no mass loss occurs at these temperatures. (B) FT-IR spectra of evolved gas at 480 °C (red) and 520 °C (blue). Apart from obvious bands due to CO_2 (3) and water (4) it is possible to identify a carbonyl stretch (2) and bands (1) that can be matched with unsaturated oxidized hydrocarbons.

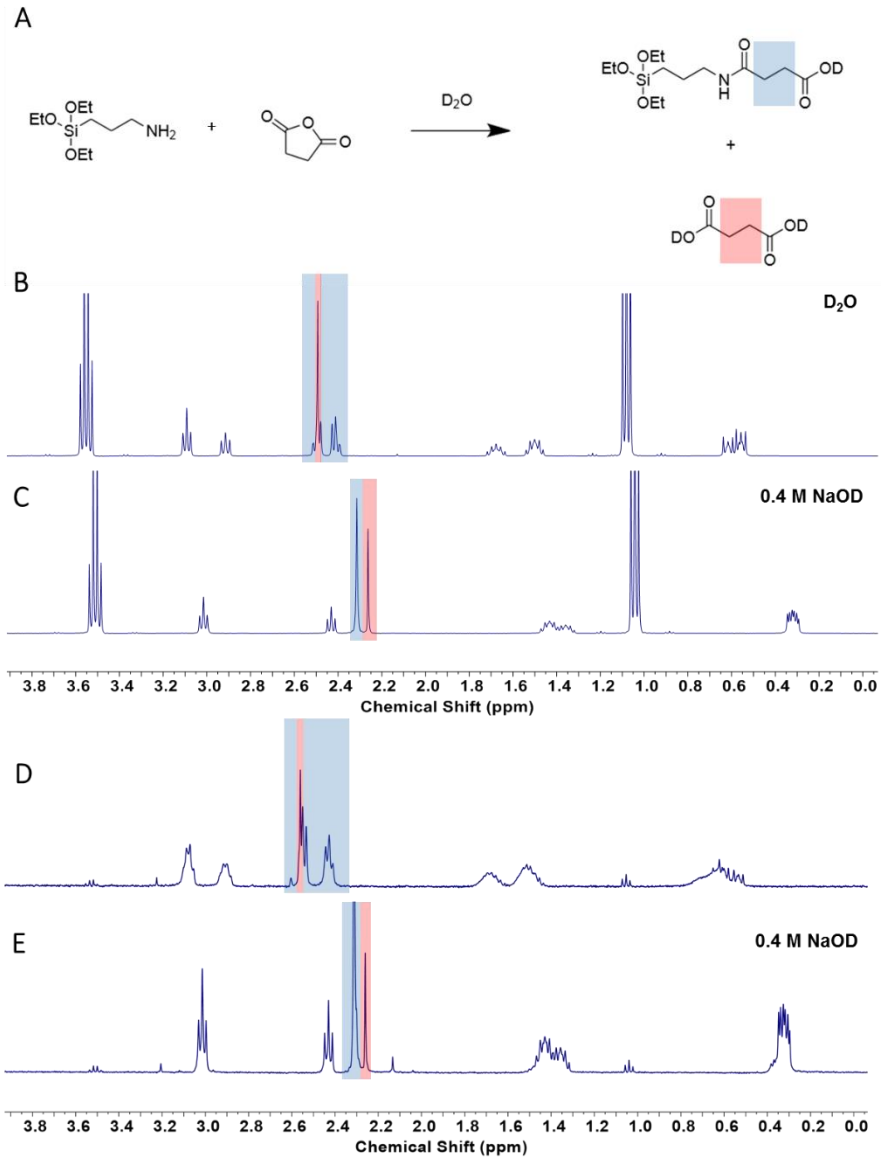

Fig. S9 (A) Scheme for reaction of APTES and succinic anhydride in 1:1 molar ratio in D_2O at room temperature. This produces a mixture of products: APTES-succinate conjugate, unreacted APTES and hydrolyzed succinic acid. The change in shape and chemical shift of their resonances can be observed in ^1H NMR spectra acquired in D_2O (B) and in NaOD 0.4 M (C). Note that two triplets (2.40 ppm and 2.49 ppm) corresponding to the conjugated succinate hydrogens collapse into a single peak (2.31 ppm) in basic environment. In both cases, the resonance of the conjugated succinate (blue) is adjacent to the resonance of free succinic acid (red). Similar observations are made in ^1H NMR spectra of the modified silica. When dissolved and measured at 0.4 M NaOD (E) the conjugated succinate resonance lacks multiplicity. However, when the sample is neutralized with DCl (D), this resonance is restored to the expected triplets. Approximately 10 % of succinate is present in the form of free acid. This is probably due to hydrolysis of the amine bond under the conditions for silica dissolution (0.4 M NaOD, 45 °C) since increasing base concentration leads to increase of the free succinate resonance (data not shown).

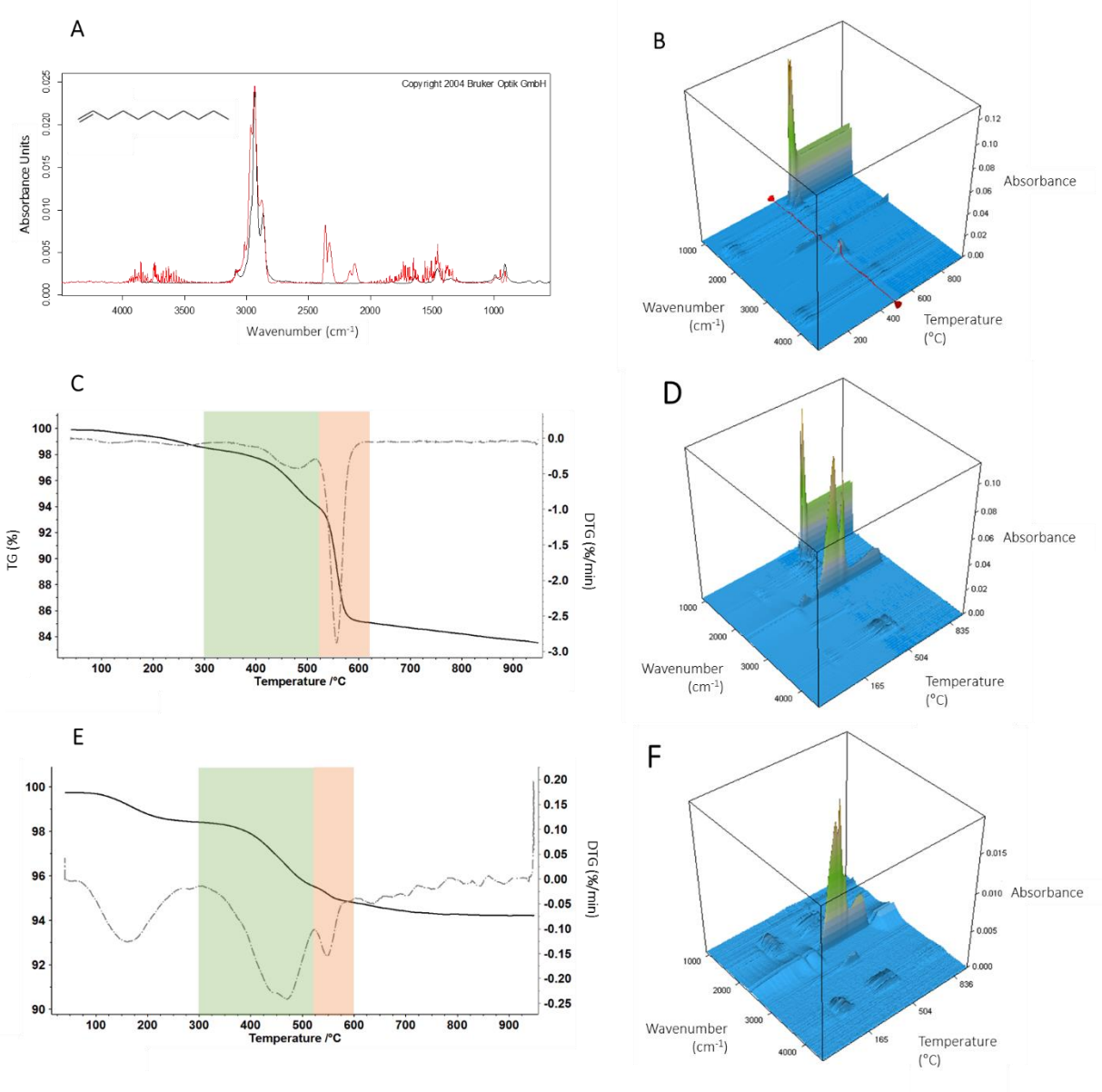

Fig. S10 (A) FT-IR spectrum at 495 °C (red) of 30 nm C_{11}COOH modified silica NPs analyzed in argon atmosphere overlaid with library FT-IR spectrum of 1-undecene (black). The absence of a carbonyl band indicates that the functional group is released in its reduced form; this is consistent with the presence of undecene bands suggesting that decarboxylation occurs prior to chain detachment from the surface. (C) The thermogram of 50 nm C_{11}COOH modified silica analyzed in argon atmosphere and the corresponding EGA-FT-IR plot (D). (E) The thermogram of 100 nm C_{11}COOH modified silica analyzed in argon atmosphere and corresponding EGA-FT-IR plot (F). The regions shaded in peach indicate the release of fluorinated compounds (possibly products of polytetrafluoroethylene decomposition) and the regions in green indicate the mass loss due to the functional group. Note that the bands similar to 1-undecene are less prominent for the 50 and 100 nm NPs, but the CO_2 bands increase in intensity.

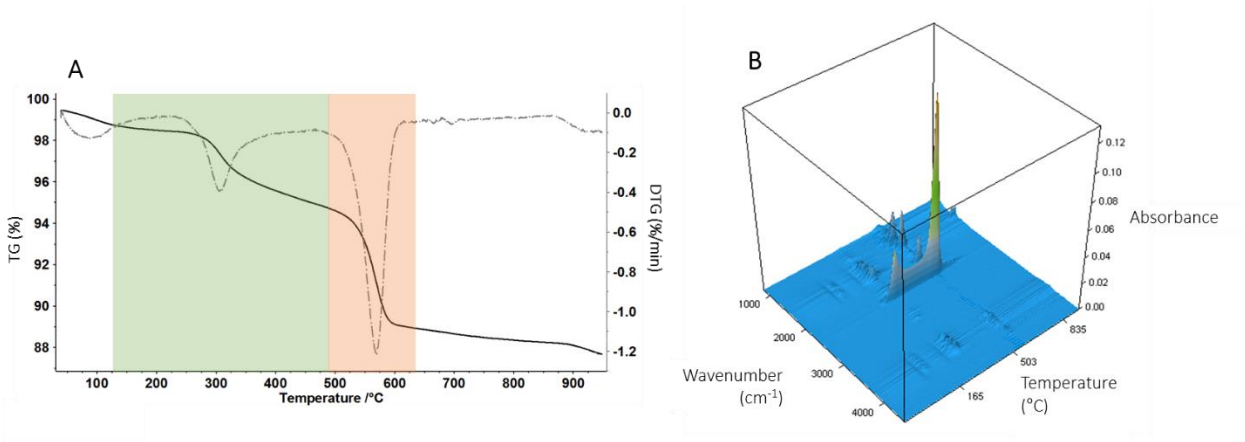

Fig. S11 (A) The thermogram of 30 nm C_{11}COOH modified silica NPs analyzed in air atmosphere with the corresponding EGA-FT-IR (B). Note that the strongest band at 1100-1250 cm^{-1} from Fig. 5b was transformed into a strong 2400-1250 cm^{-1} CO_2 band at 570 °C.

Table S2 Quantification of the C_{11}COOH functional group on 30 nm silica NPs using TGA and qNMR.

TGA conditions	TGA [with correction for bare] (µmol/g)	TGA [without correction for bare] (µmol/g)	qNMR (µmol/g)
Argon 10 °C/min	133	192	210 +/- 1
Air 10 °C/min	125	161	
Air 2 °C/min	148	189	

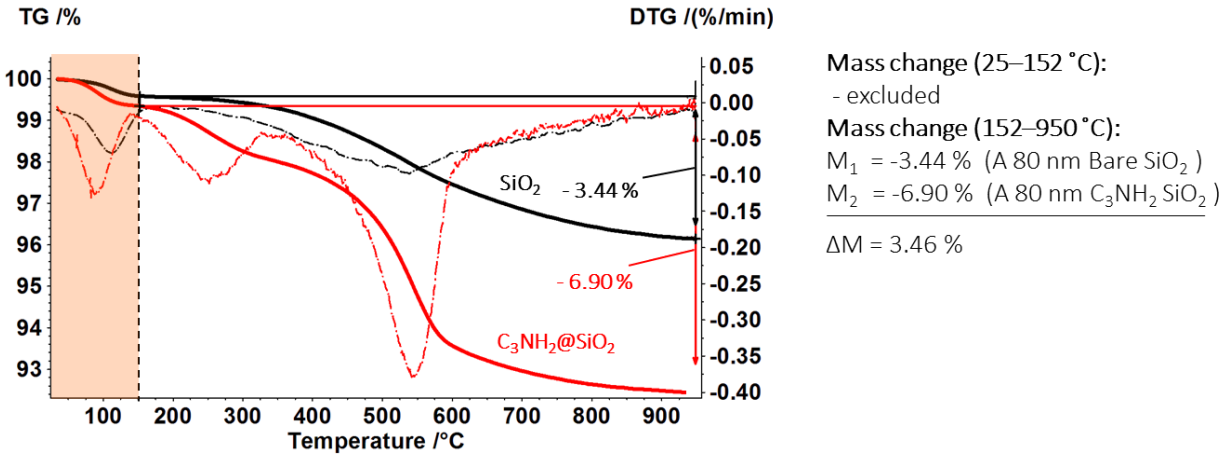

Fig. S12 An example of the correction for the mass loss for unfunctionalized silica particles. Bare sample (black) is overlaid with functionalized sample (red). Firstly, the region corresponding to the surface water removal is identified in both thermograms. This region ranges from 25 ˚C up to the temperature after which the rate of initial mass loss reaches a minimum, which should be similar in both samples. In this case 25-152 ˚C is assumed to correspond to water loss. The mass loss in the initial part of the thermogram is then excluded from the calculation. The mass loss of functionalized sample (-6.90 %) in the remaining part of thermogram (152-950 ˚C) is then corrected for the mass loss of the bare sample (3.44 %) over the same temperature range.