Supporting information

Mesoporous organosilica nanoparticles containing superacid and click functionalities leading to cooperativity in biocidal coatings

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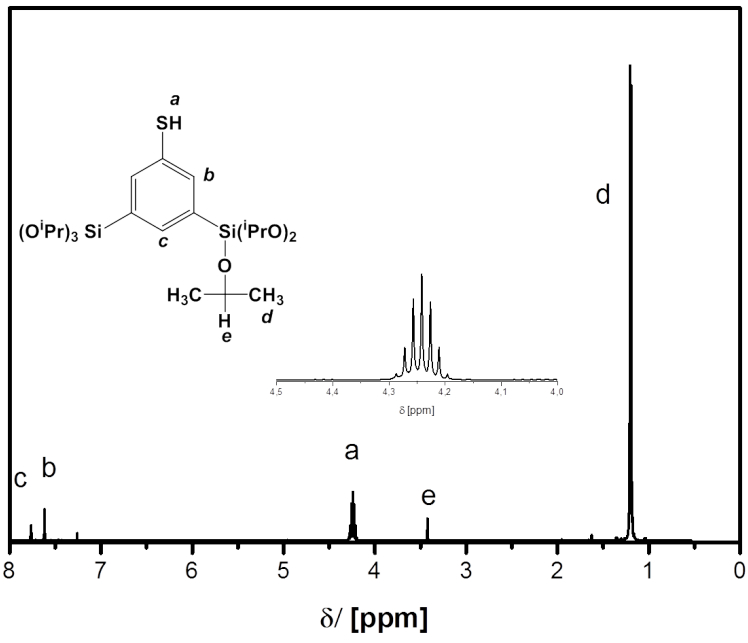
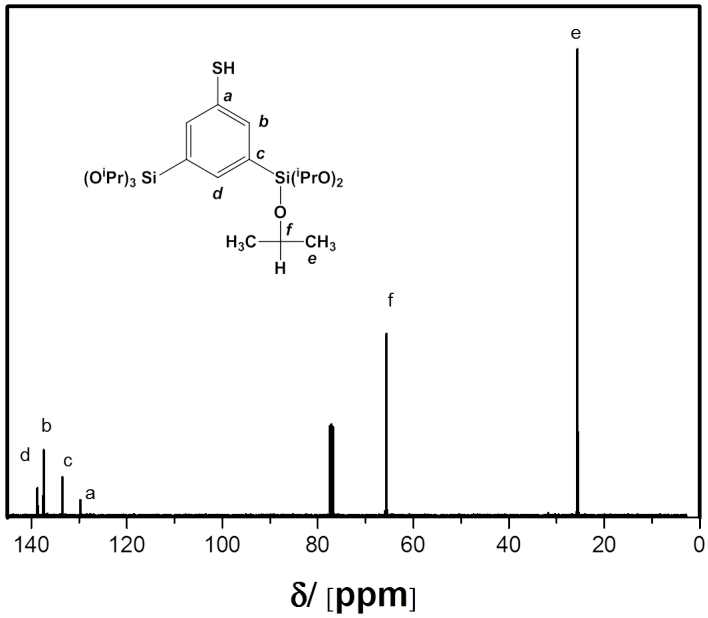
Figure S1: Characterization of the novel PMO precursor (3) 1,3-bis-tri(isopropoxysilyl)-thiophenol.

NMR data

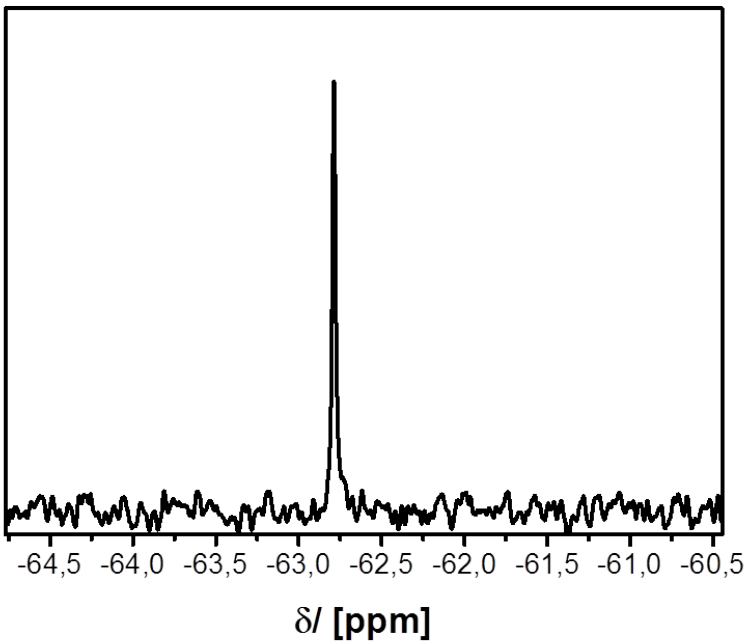
^{1}H NMR in $CDCl_3$



^{13}C NMR in *CDCl$_3$*



^{29} Si NMR in *CDCl$_3$*



ESI-MS data

Black: Experimental data

Grey: Simulated spectrum for 1,3-bis-tri(isopropoxysilyl)-thiophenol

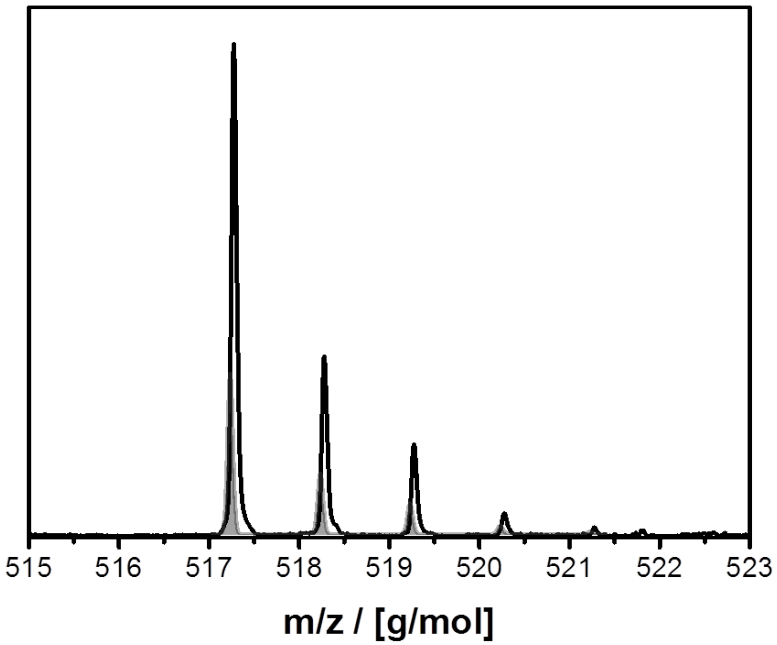
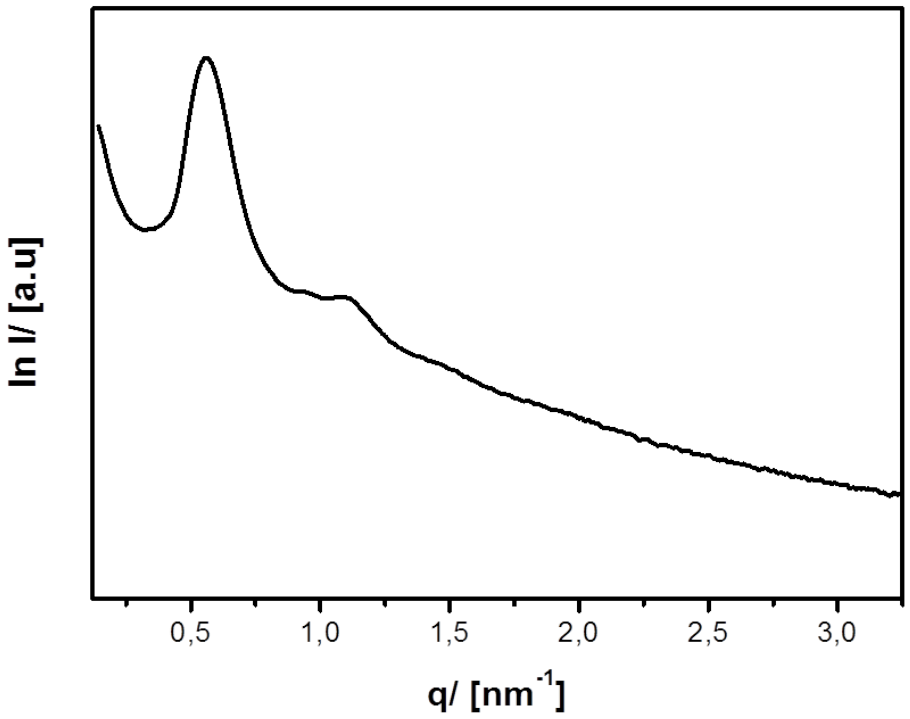
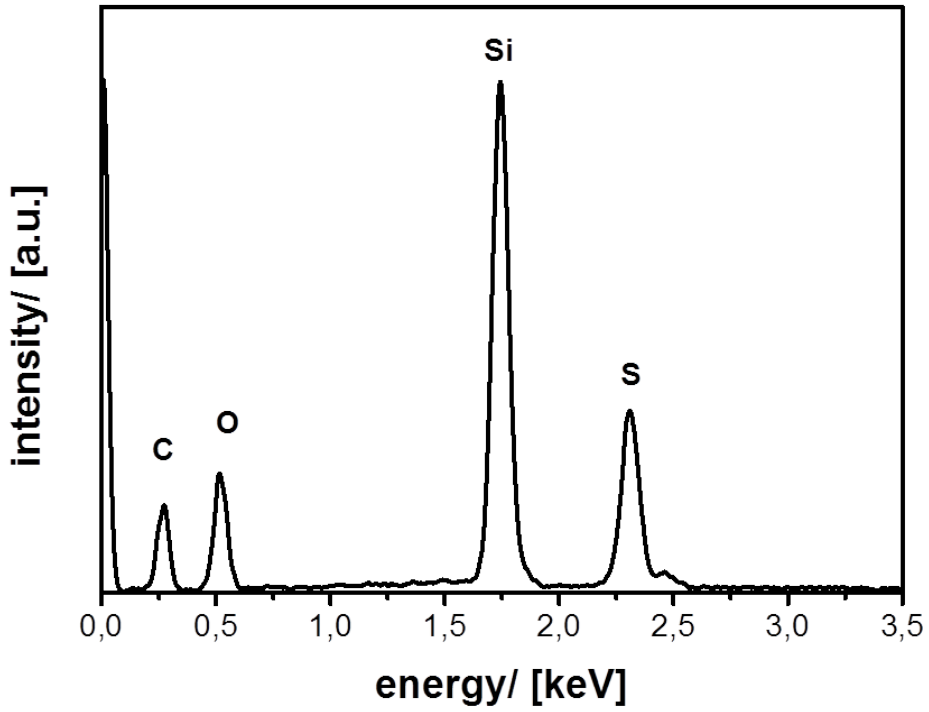


Figure S2: Additional analytical data for the novel PMO material UKON-2j.

SAXS

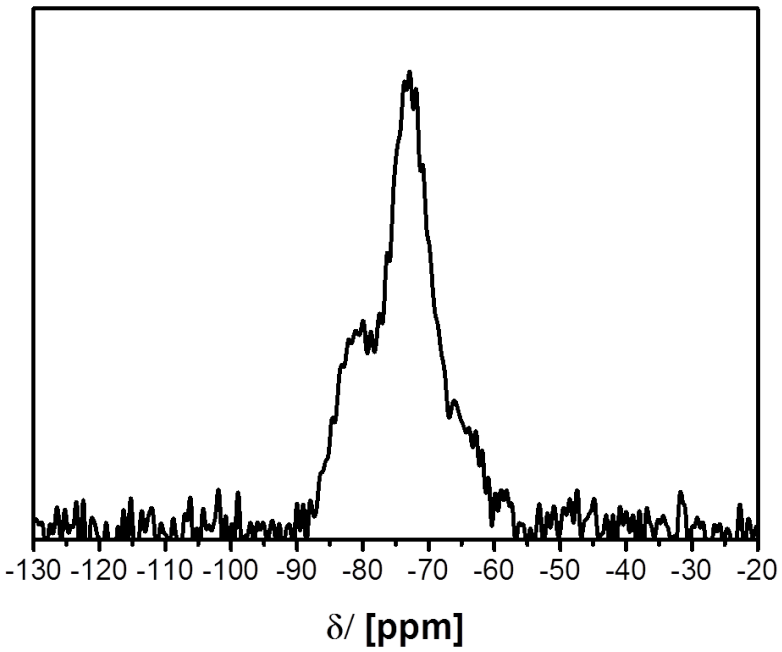


EDX data



NMR data

^{29}Si MAS NMR



^{13}C MAS NMR

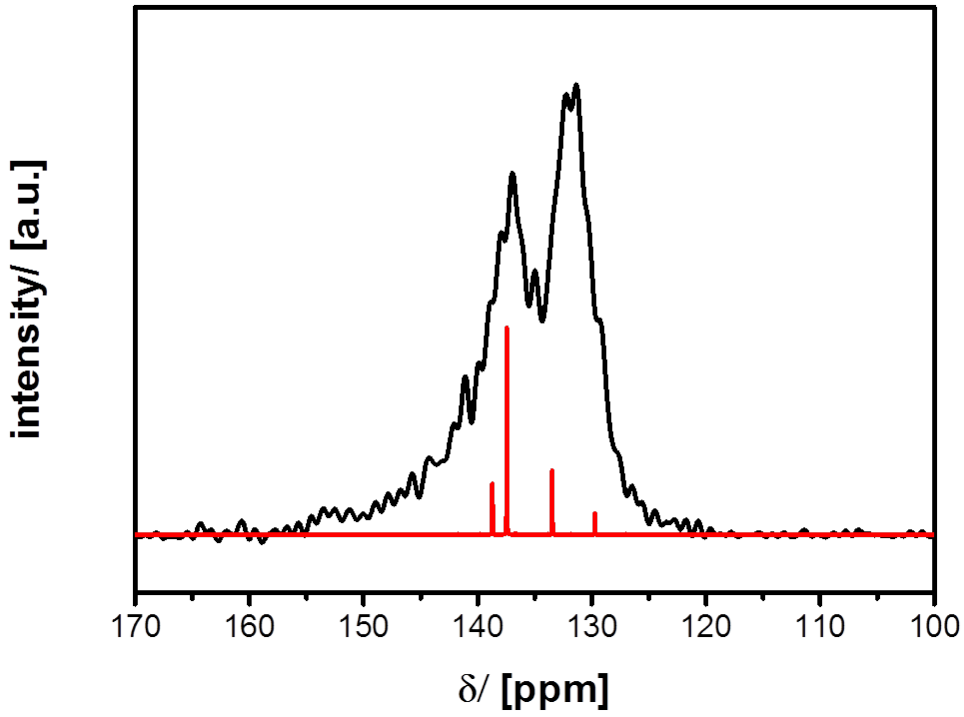
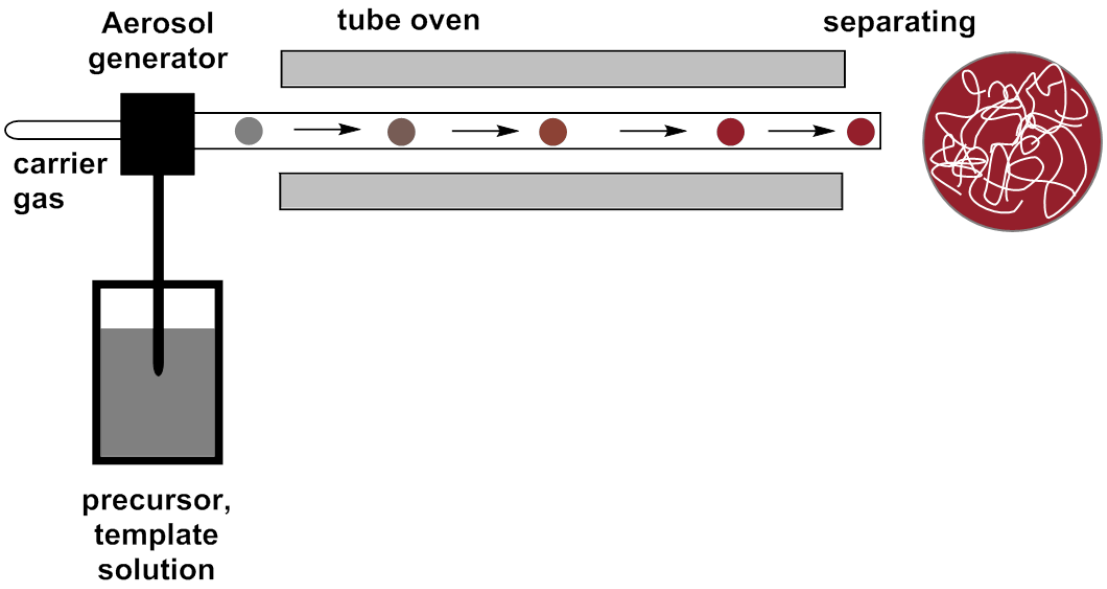
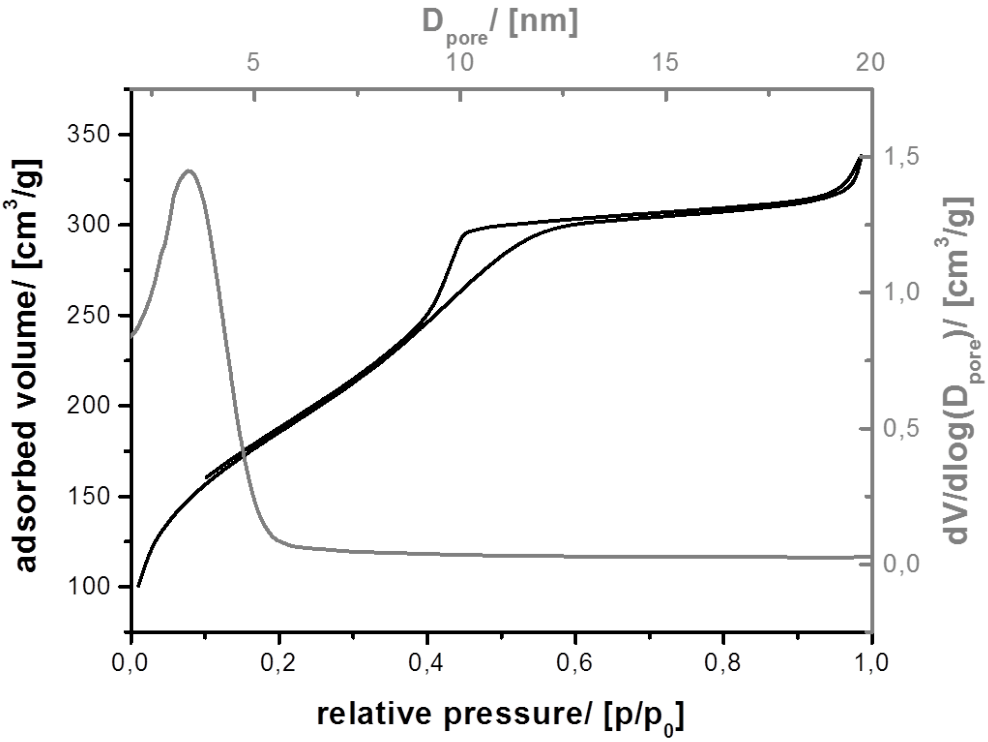


Figure S3: Collected data for UKON-2j nanoparticles prepared via the aerosol-assisted route.

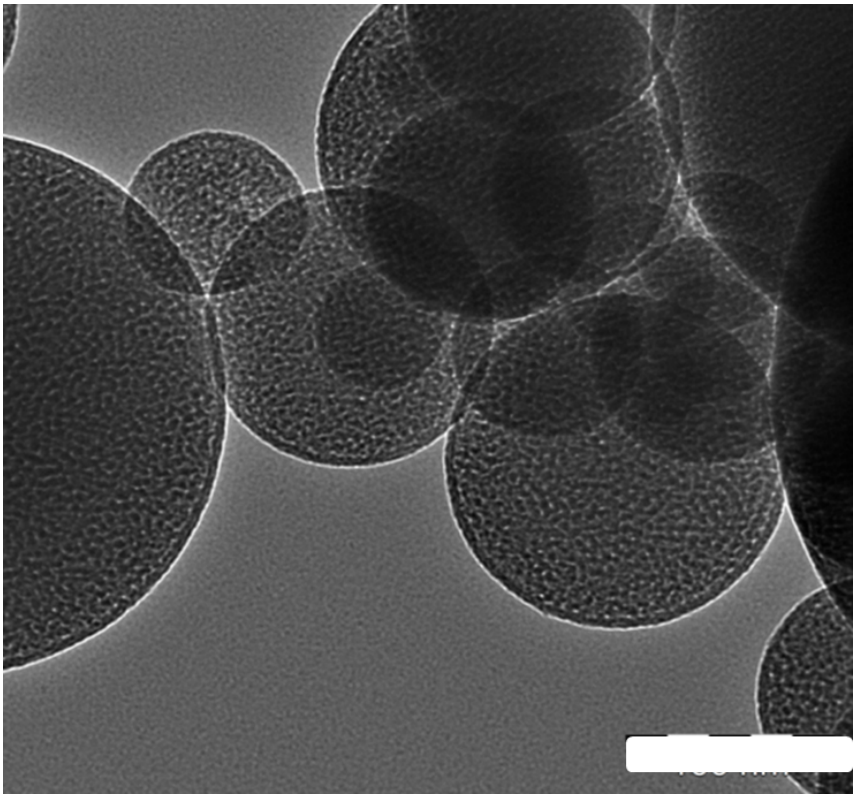
(a) Experimental set-up used for the EISA preparation of mesoporous particles of the UKON-type.



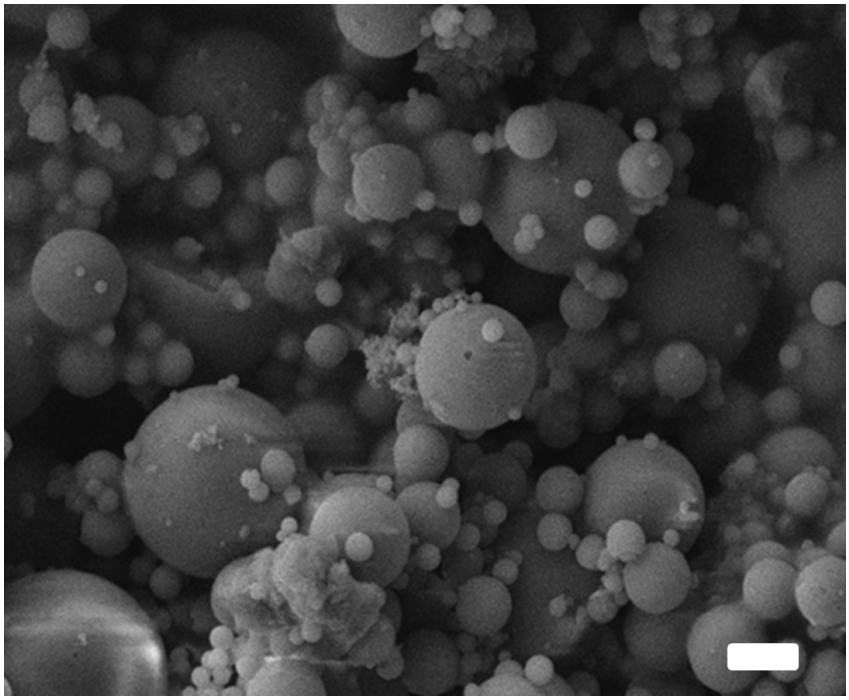
(b) N_2 physisorption data of UKON-SH np; BET 670m^2/g; pore diameter: 3.4 nm.



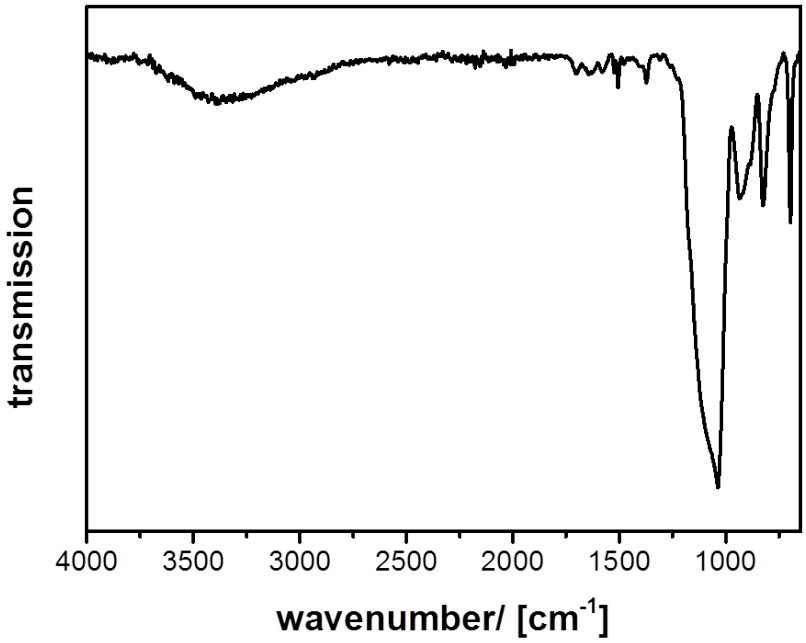
(c) TEM data of UKON-2j np; scale bar = 100 nm



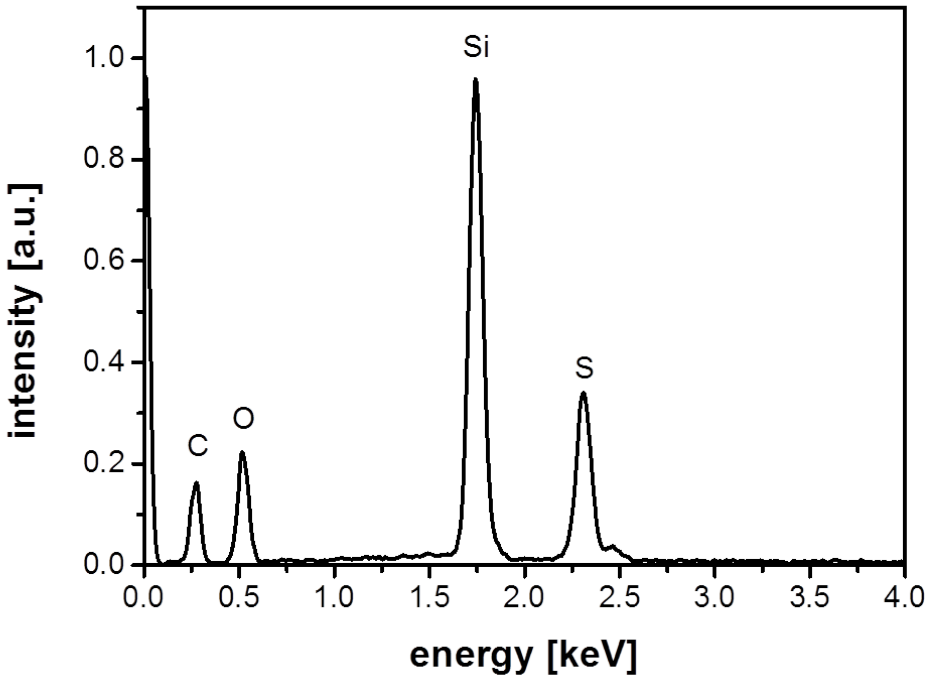
(d) SEM data of UKON-2j; scale bar = 1µm



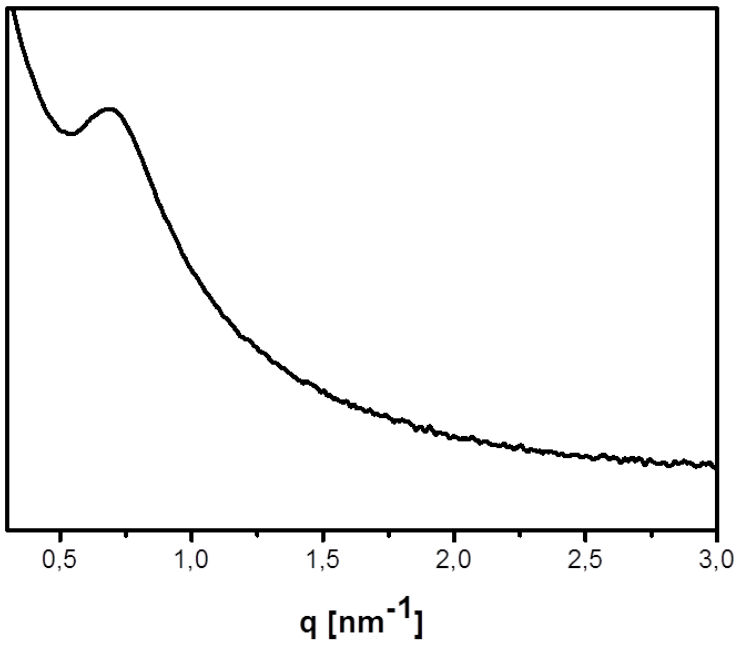
(e) IR data of UKON-2j np



(f) EDX data of UKON-2j np: Si:S 2:1



(g) SAXS data of UKON-2j np



(h) ^{29}Si MAS NMR data of UKON-2j np

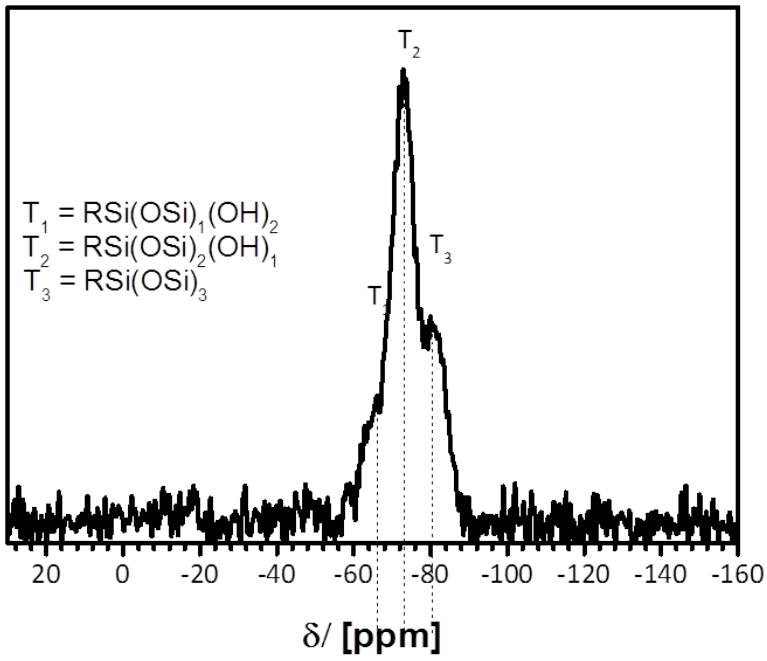
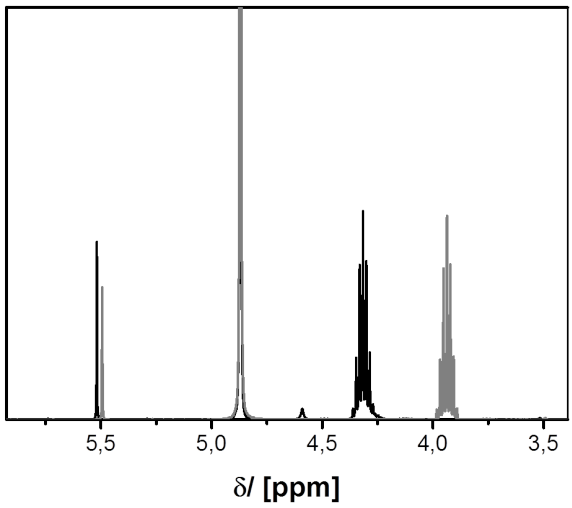


Figure S4: Investigation of the pre-hydrolysis using NMR spectroscopy.

^{1}H NMR data in MeOD of 1,5-bis-tri(isopropoxysilyl)-thiophenol (3)

Black: before hydrolysis

Grey: after 3 h of hydrolysis



^{1}H NMR data in MeOD of 1,5-bis-tri(isopropoxysilyl)-benzene-3-sulfonyl chloride (2)

Black: before hydrolysisin MeOD (MeOD hydrolyzed compound (2) within minutes!)

Grey: after 10 min of hydrolysis

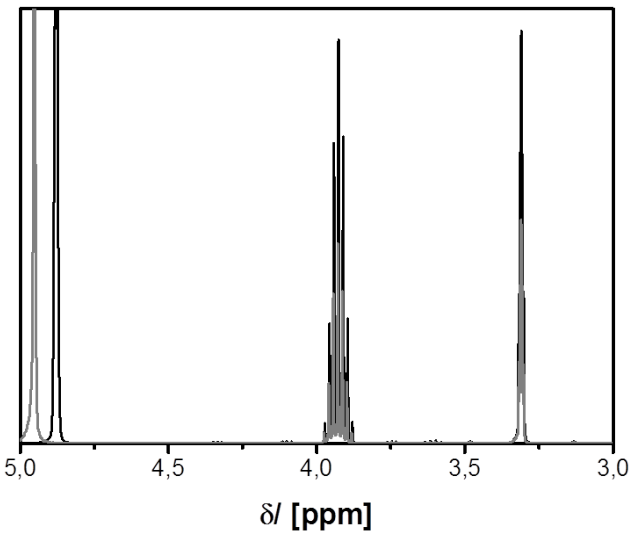
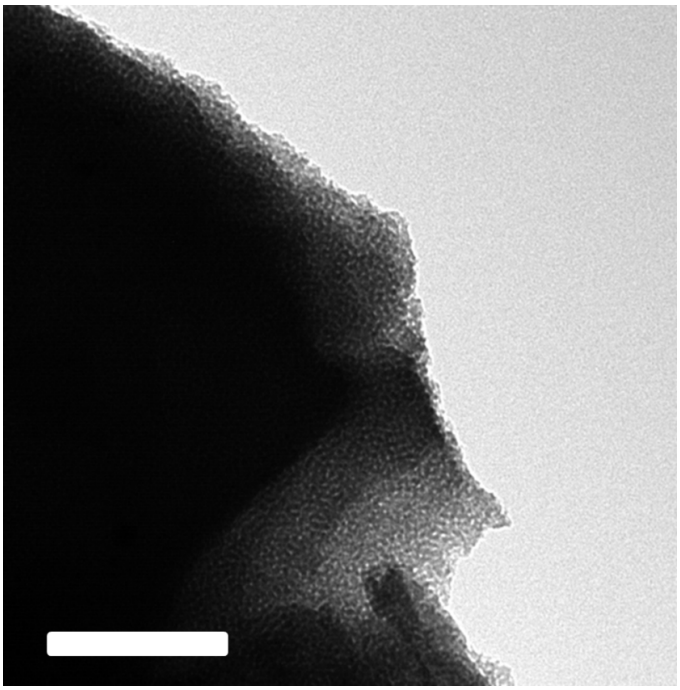


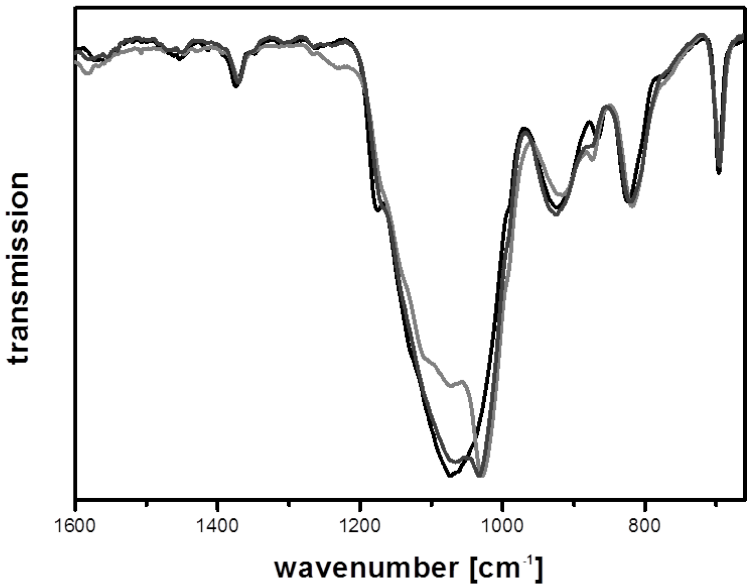
Figure S5: Collected analytical data for bifunctional, mesoporous organosilica materials.

(a) PMO materials in powder form.

TEM data of UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5



FT-IR data of UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5



Black: UKON-2j np

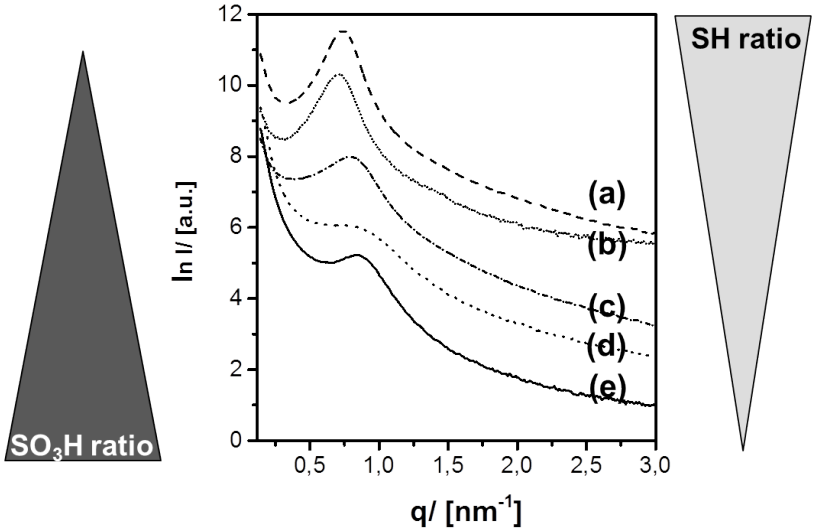
Light grey: UKON-2i np

Dark grey: of UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5

SAXS data

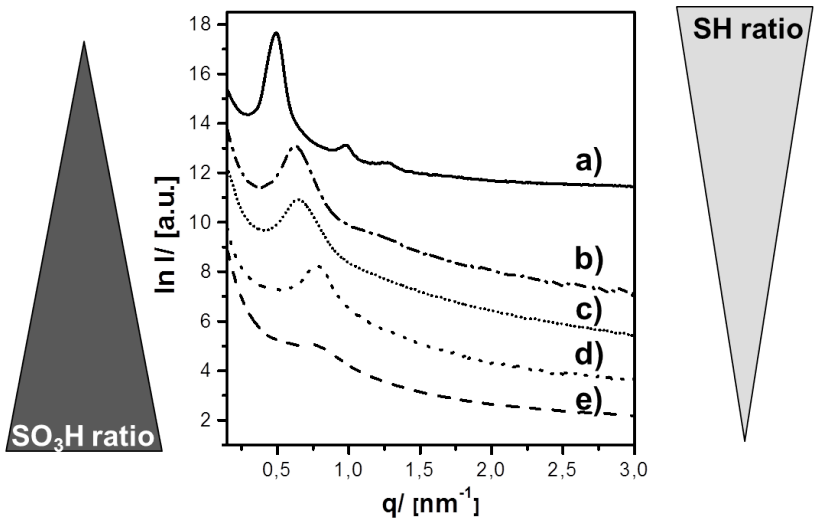
UKON (SH-PhSi2O3)1-x(SO3H-PhSi2O3)x synthesized with Pluronic P123

(a) UKON -2j
(b) UKON (SH-PhSi2O3)0.75(SO3H-PhSi2O3)0.25
(c) UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5
(d) UKON (SH-PhSi2O3)0.25(SO3H-PhSi2O3)0.75
(e) UKON-2i



UKON (SH-PhSi2O3)1-x(SO3H-PhSi2O3)x synthesized with Pluronic F127

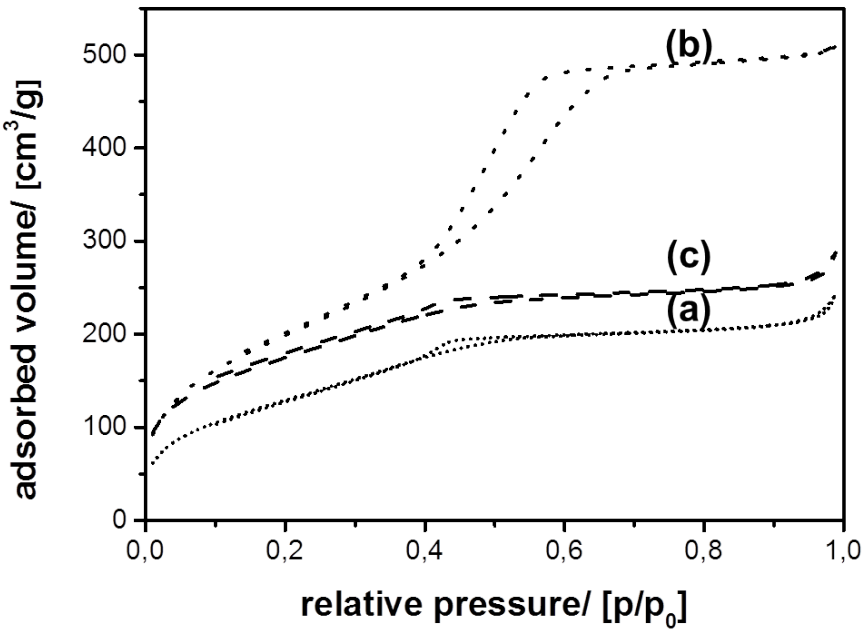
(a) UKON -2j
(b) UKON (SH-PhSi2O3)0.75(SO3H-PhSi2O3)0.25
(c) UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5
(d) UKON (SH-PhSi2O3)0.25(SO3H-PhSi2O3)0.75
(e) UKON-2i



N_2 physisorption

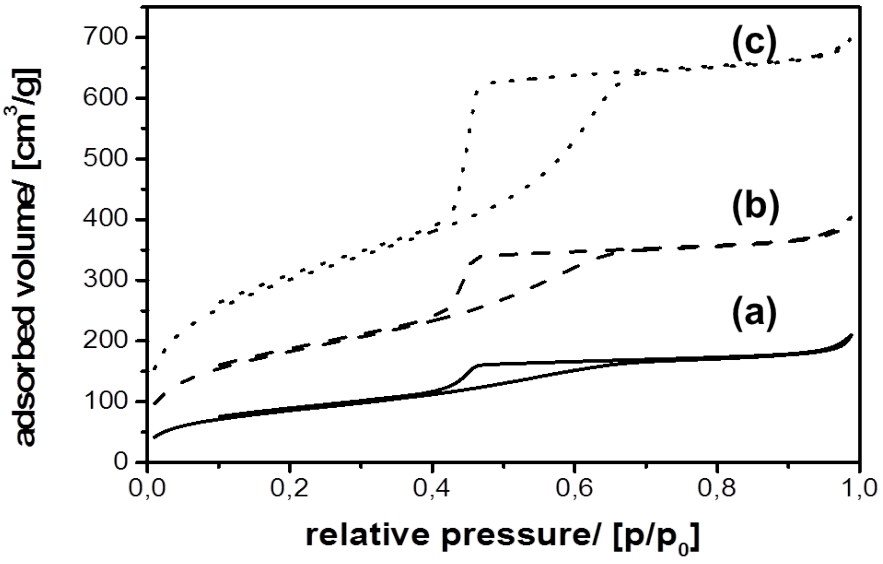
UKON (SH-PhSi2O3)1-x(SO3H-PhSi2O3)x synthesized with Pluronic P123

(a) UKON (SH-PhSi2O3)0.75(SO3H-PhSi2O3)0.25
(b) UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5
(c) UKON (SH-PhSi2O3)0.25(SO3H-PhSi2O3)0.75



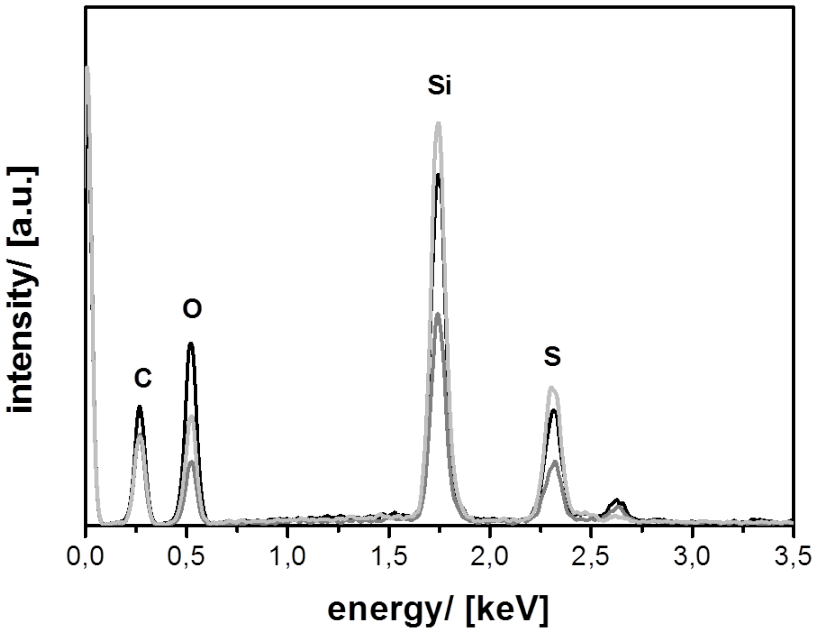
UKON (SH-PhSi2O3)1-x(SO3H-PhSi2O3)x synthesized with Pluronic F127

(a) UKON (SH-PhSi2O3)0.25(SO3H-PhSi2O3)0.75
(b) UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5
(c) UKON (SH-PhSi2O3)0.75(SO3H-PhSi2O3)0.25



EDX of bifunctional PMO:

UKON (SH-PhSi2O3)0.75(SO3H-PhSi2O3)0.25 (light grey)	Si:S 2:1
UKON (SH-PhSi2O3)0.5(SO3H-PhSi2O3)0.5 (grey)	Si:S 2:1.1
UKON (SH-PhSi2O3)0.25(SO3H-PhSi2O3)0.75 (black)	Si:S 2:0.9

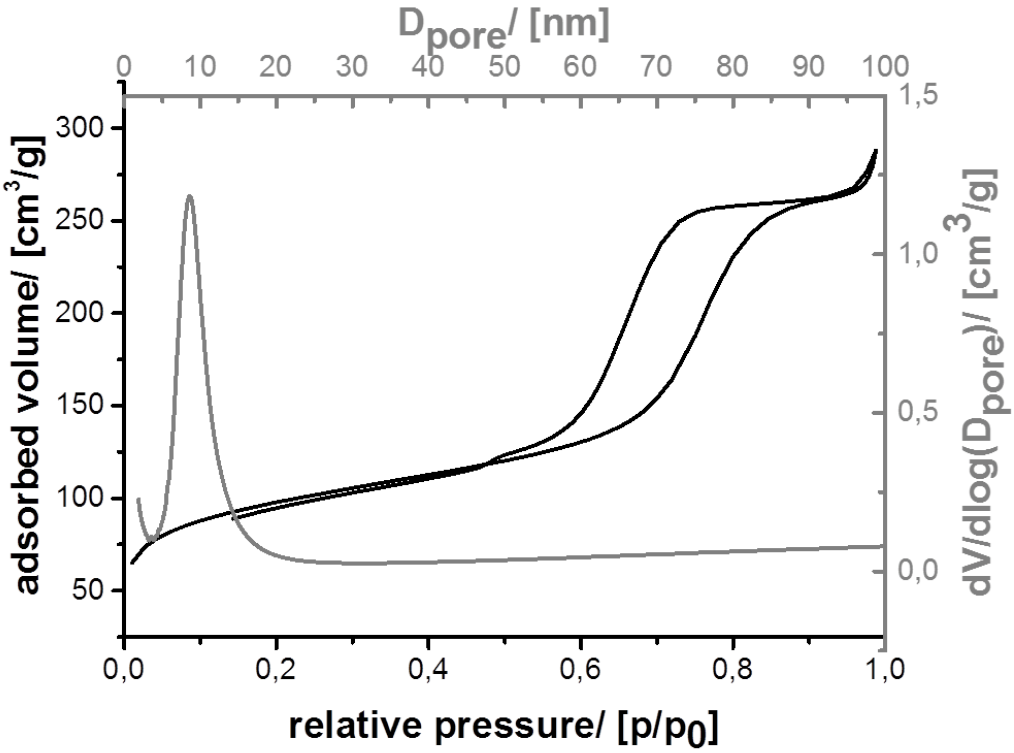


(b) Nanoparticles obtained via the aerosol approach.

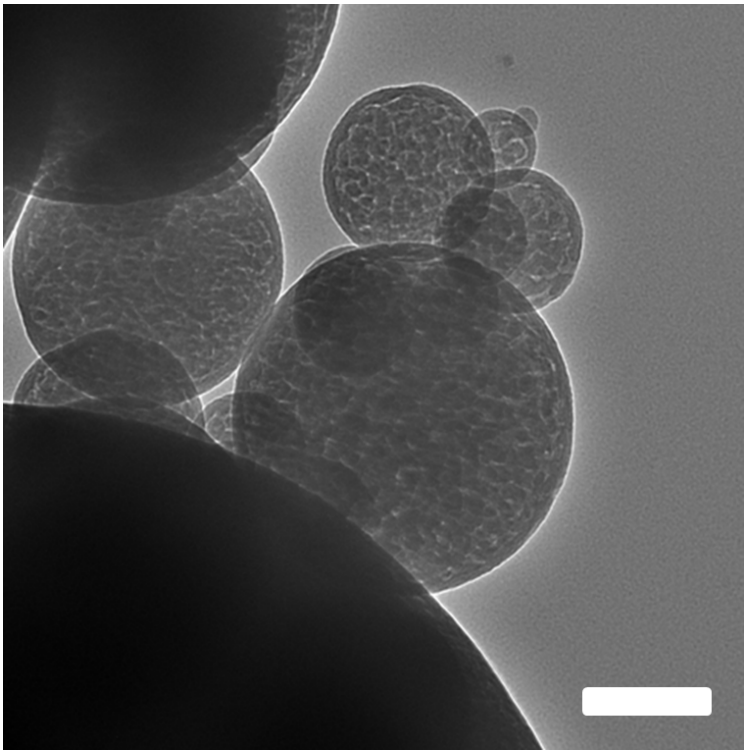
SH100 material (UKON-2j): see S-3

SH50 material:

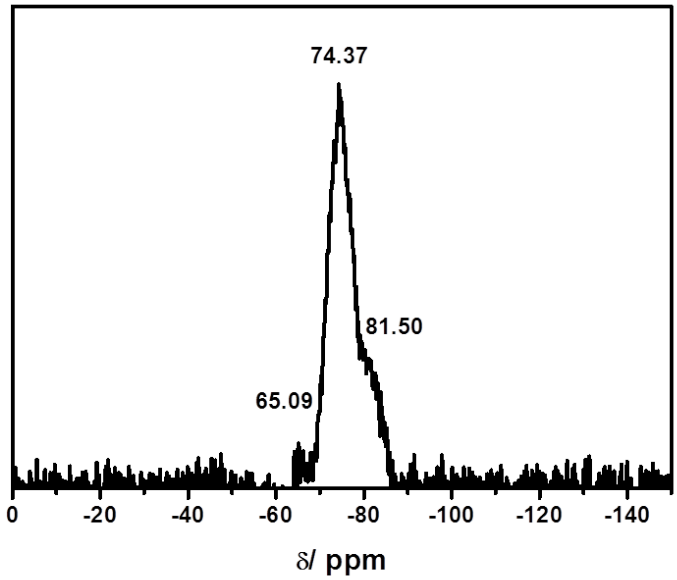
N_2 physisorption data: BET 350 m^2/g; pore diameter: 8.6 nm



TEM data; scale bar = 100 nm

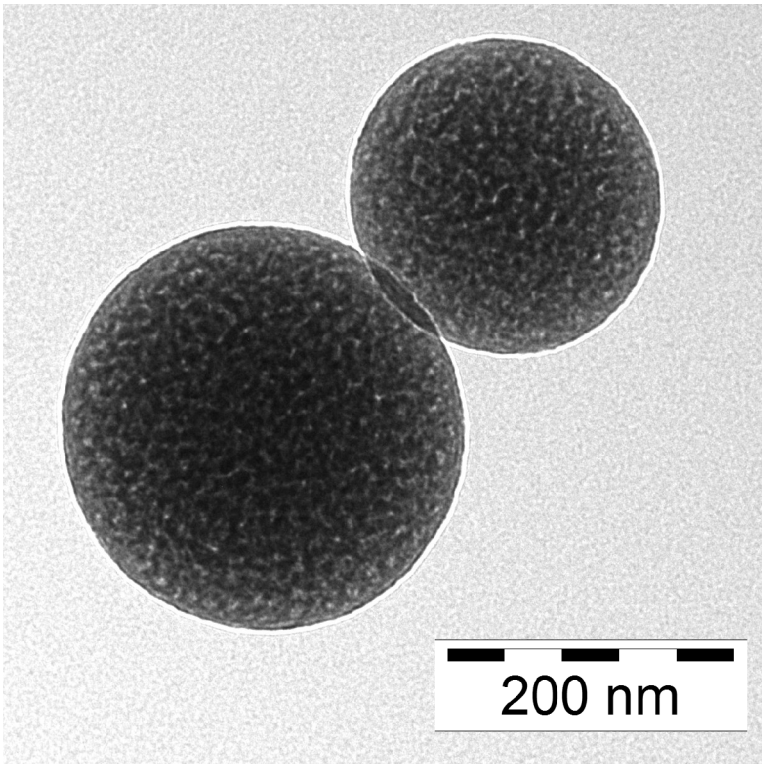


^{29}Si MAS

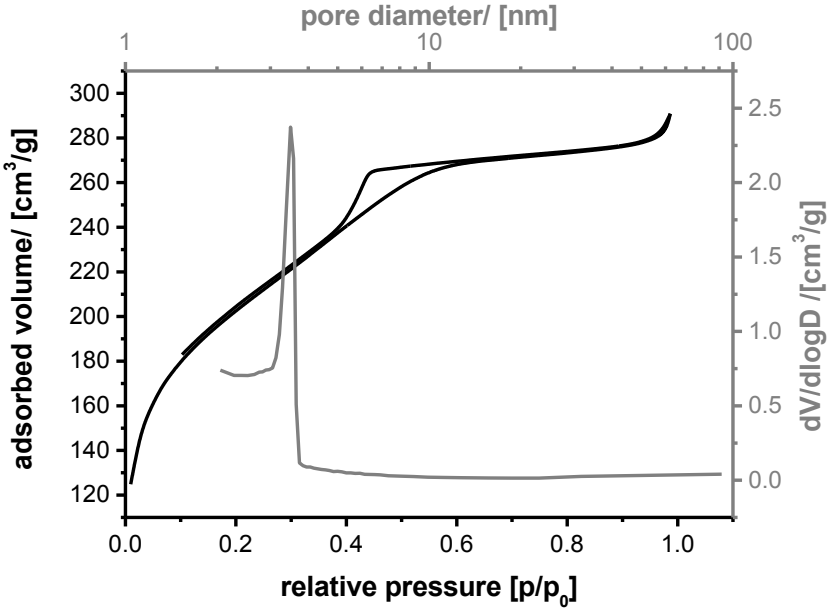


SO_3H100 material (UKON 2-i):[1]

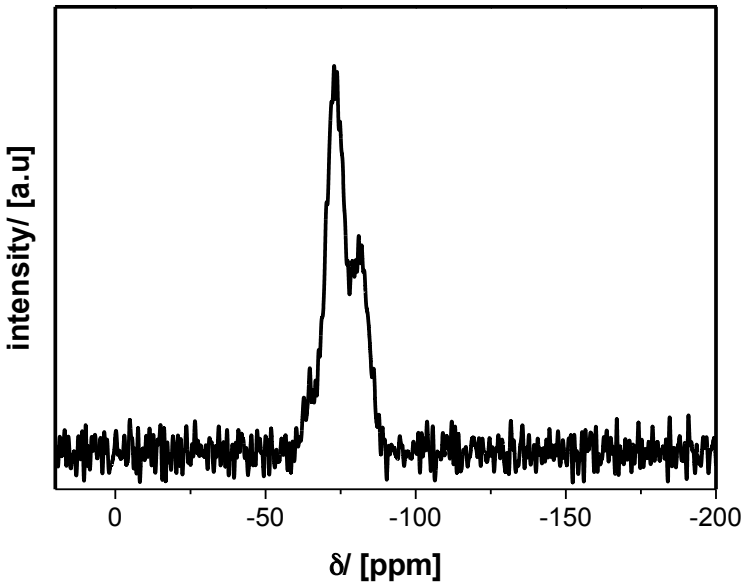
TEM:



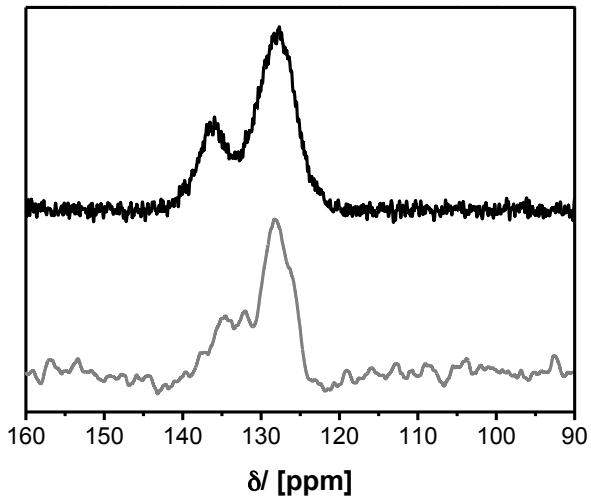
N_2 physisorption isotherm and BJH pore-size distribution function:



Solid-state ^{29}S-NMR:



solid-state ^{13}C-NMR:



black graph ≅ UKON-2i powder

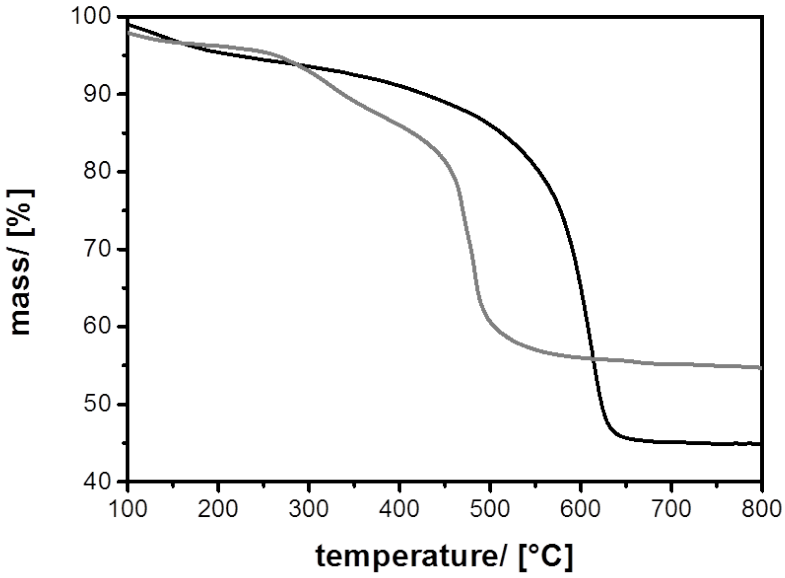
grey graph ≅ UKON-2i nanoparticles

Figure S6: Silver ion Ag^+ loading and release.

TGA UKON-2i np

UKON-2i (black) *remaining mass 45%*

UKON-2i @Ag^+ (grey) *remaining mass 55%*



TGA UKON-2j np

UKON-2j (black) *remaining mass 52%* vs

UKON-2j @Ag^+ (grey) *remaining mass 61%*

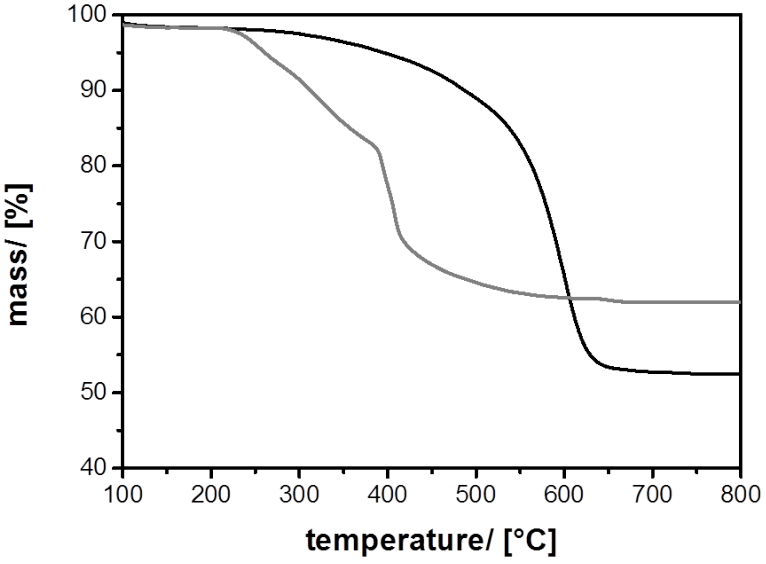


Table of Ag^+ content on different PMO materials

SH [%]	SO_3H [%]	ratio S: Ag day 0	ratio S: Ag day 5	Ag release EDX [%]	Ag release ISE [mg/l*m^2]
100	0	1: 0.9	1: 0.8	22	0.2
75	25	1: 0.65	1: 0.35	56	0.03
50	50	1:0.6	1: 0.3	50	1.8
25	75	1:0.8	1: 0.3	63	2.5
0	100	1: 0.95	1:0.1	90	12.04

<u>EDX of bifunctional PMO hosting Ag^+:</u>

EDX spectra after adsorption of Ag^+ in different mesoporous materials: stirring in water for 9

red graphj ≅ Ag^+ @ UKON-2j

black graph ≅ Ag^+ @ SH50

blue graph ≅ Ag^+ @ UKON-2i

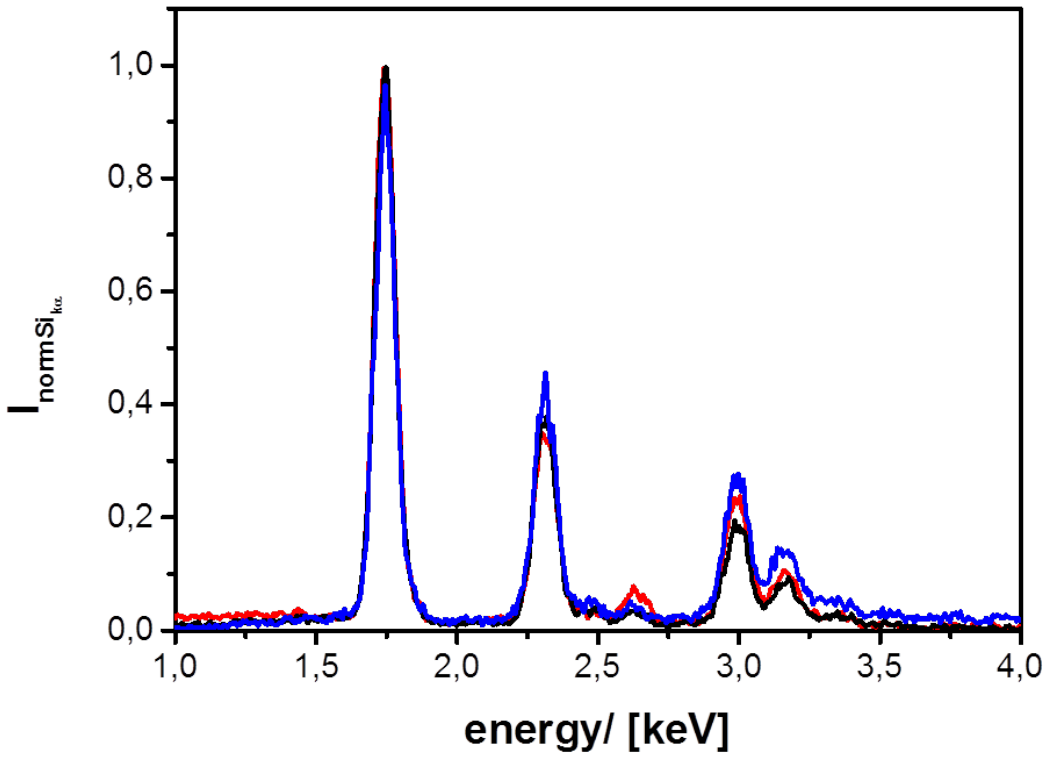
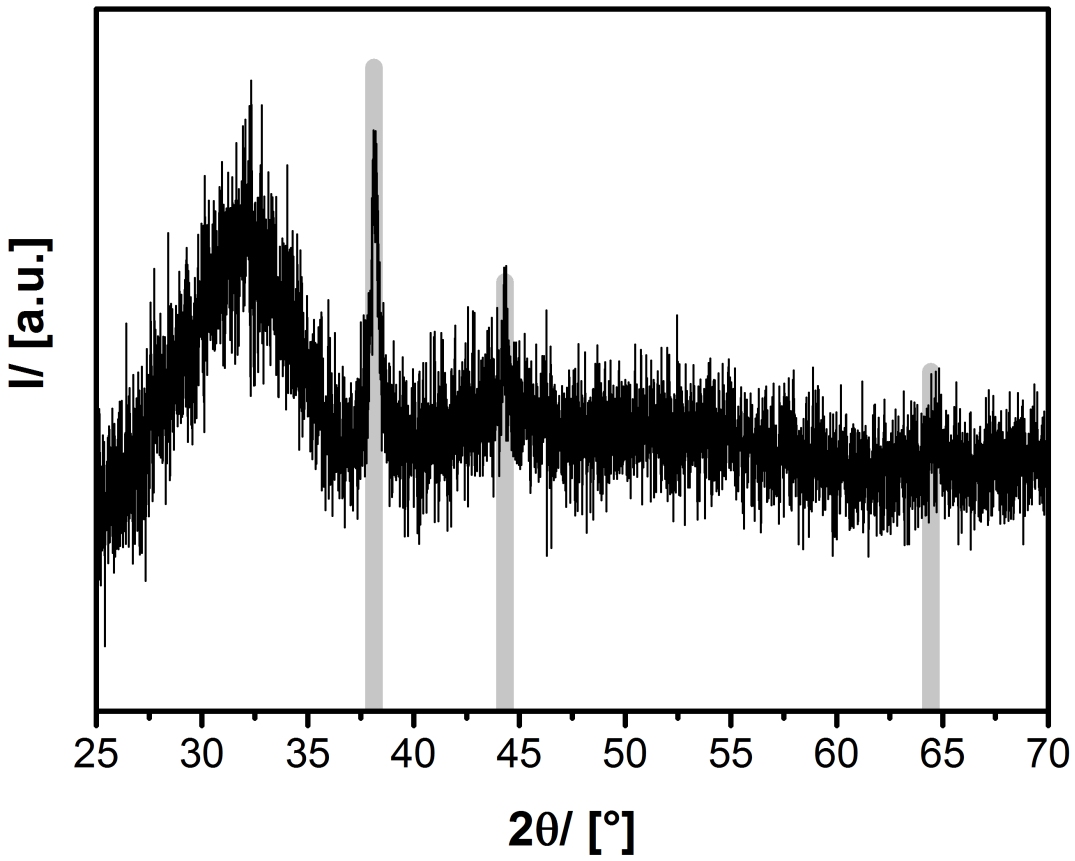


Figure S7: PXRD measurement of Ag^0@SH50



black graph ≙ experimental pattern (background corrected)

grey bars ≙ diffraction signals expected for metallic silver (Ag^0)

The broad signal at 32° 2θ originates from the amorphous organosilica matrix.

Figure S8: N_2 physisorption data of Ag^0@ UKON-SH np; BET 340m^2/g; pore diameter: 2.4 nm.

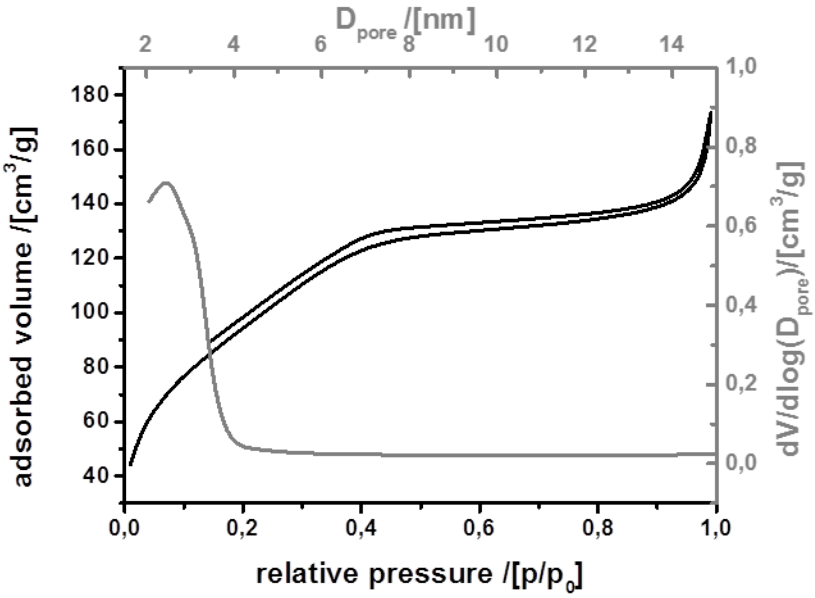
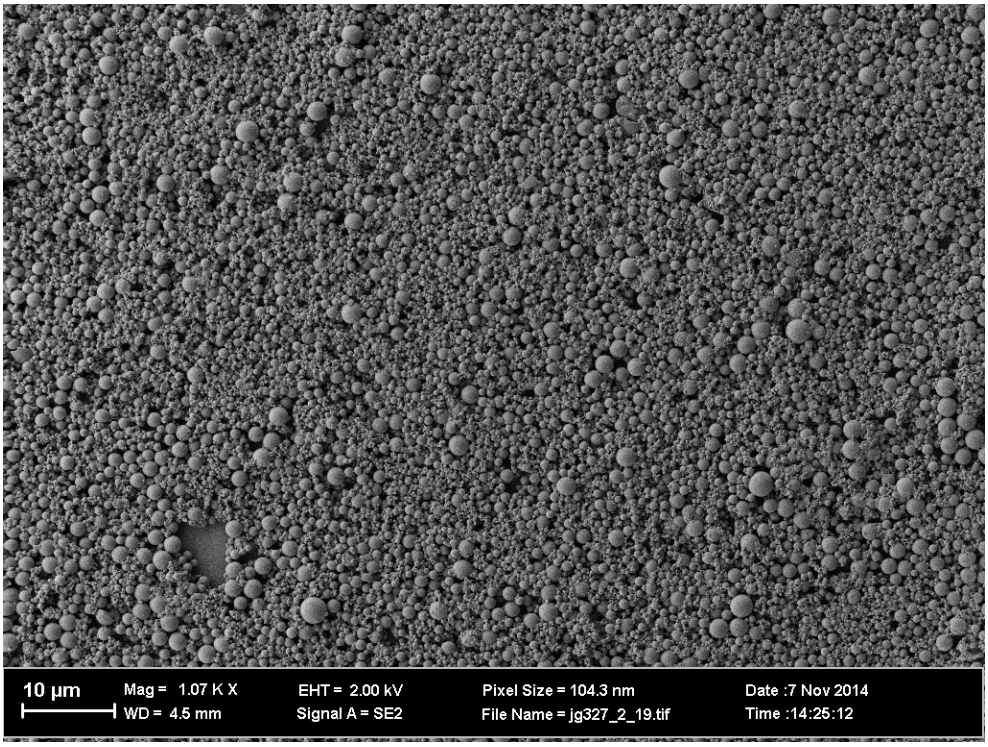
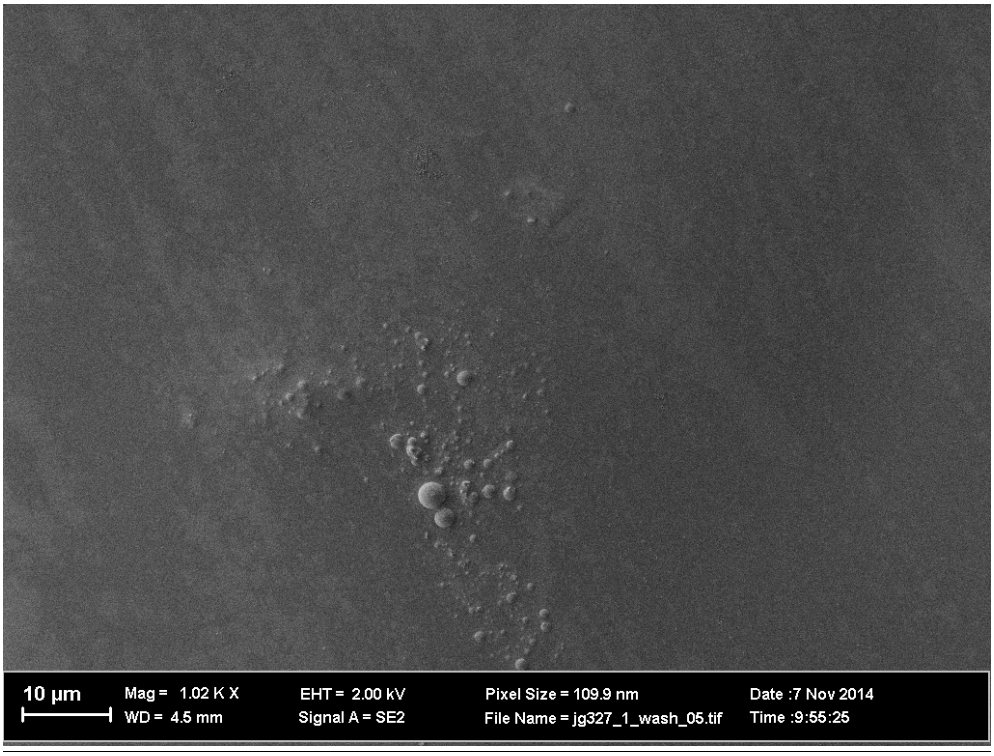


Figure S9: SEM data for immobilization experiments on glass surfaces (reference systems).

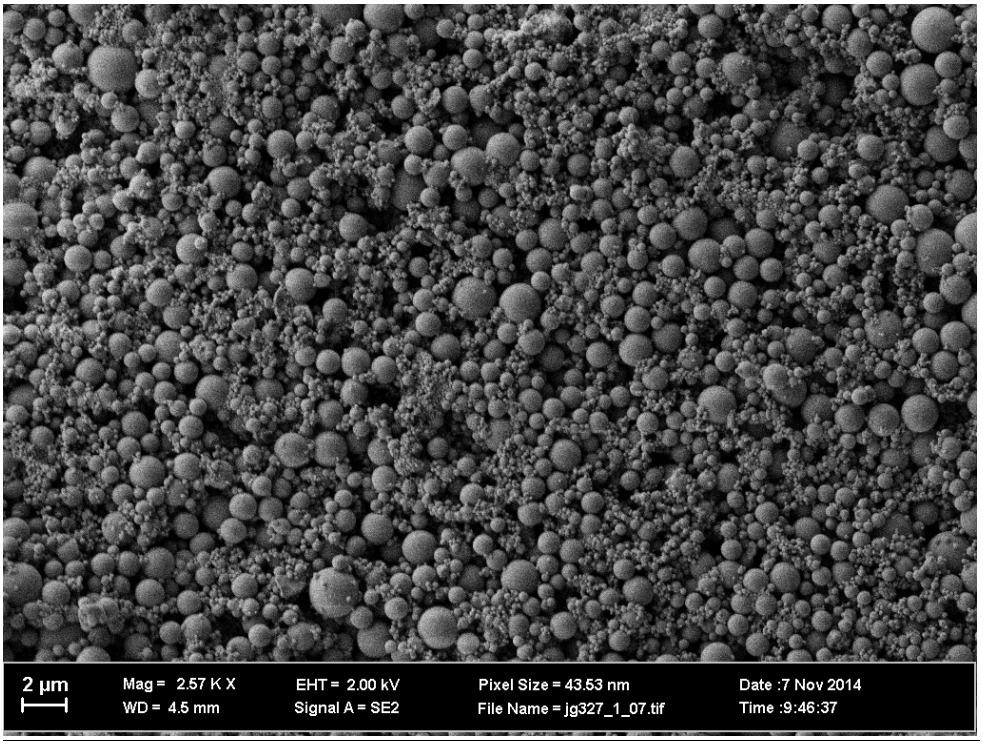
SO_3H100 before washing:



SO_3H100 after washing:



SiO_2 particles before washing:



SiO_2 particles after washing:

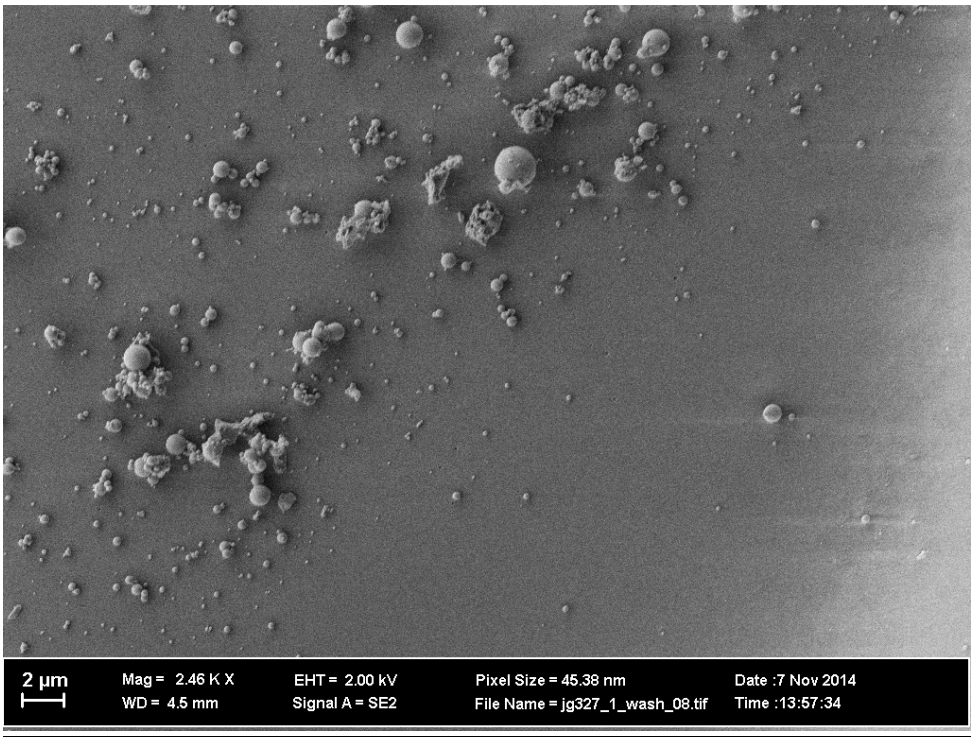
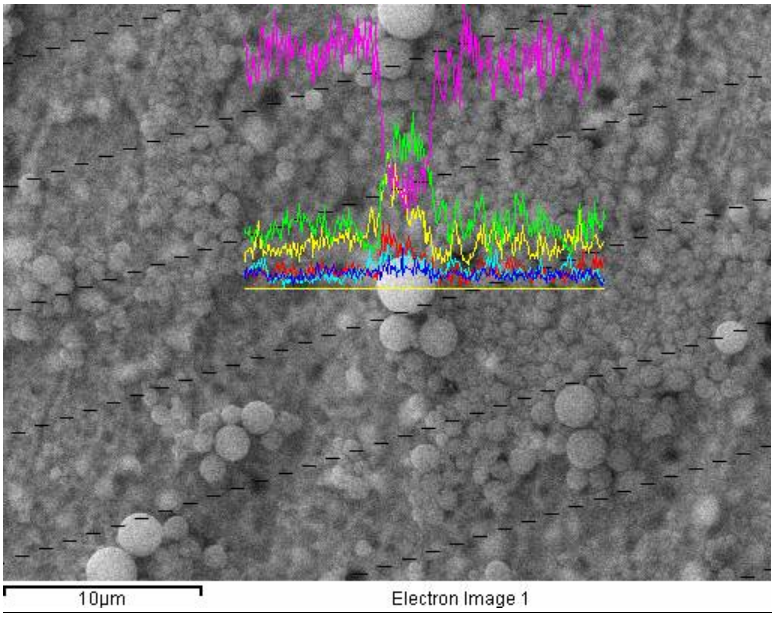


Figure S10: SEM/EDX data for immobilization of SH50 particles on stainless steel surfaces.



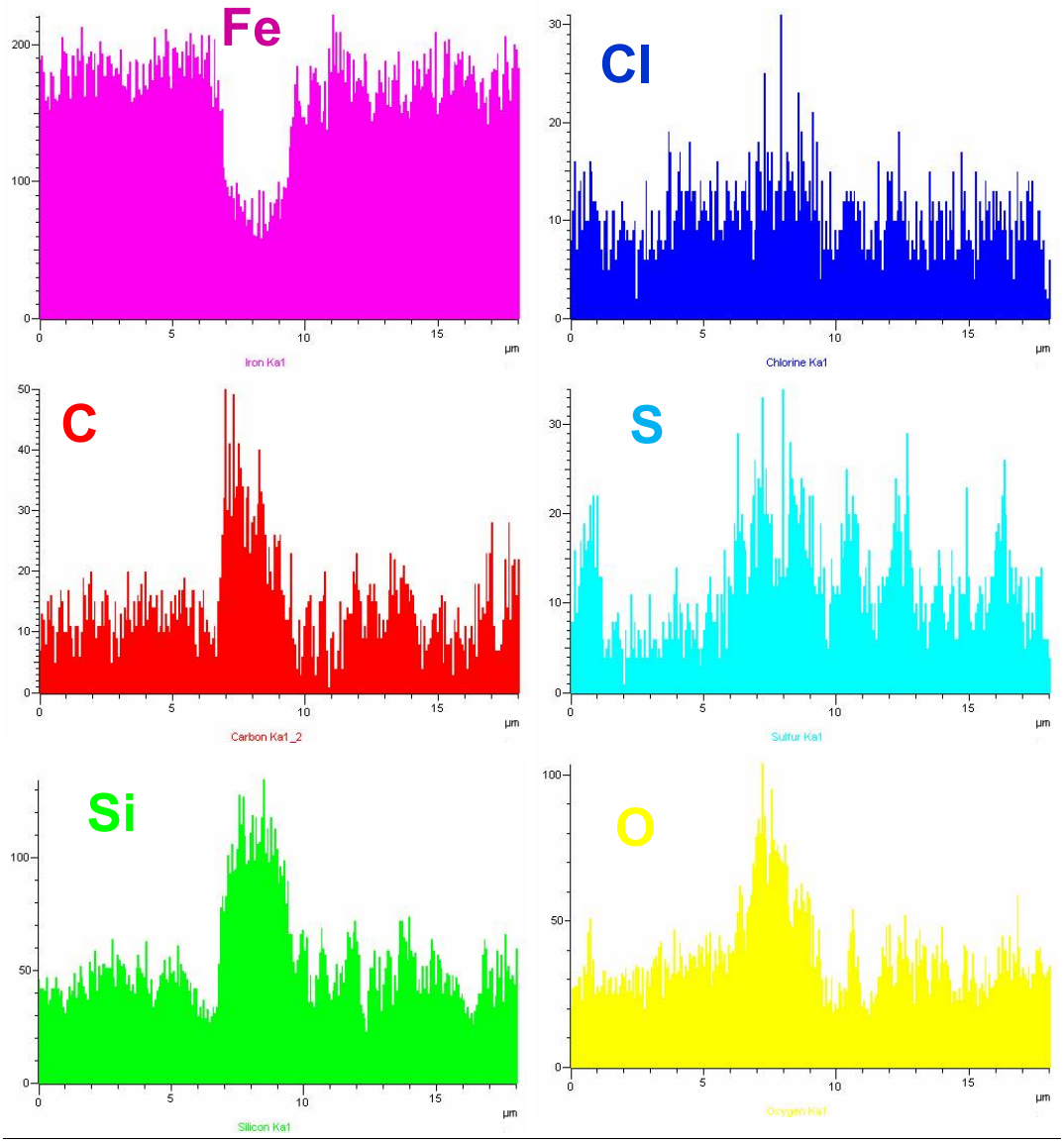
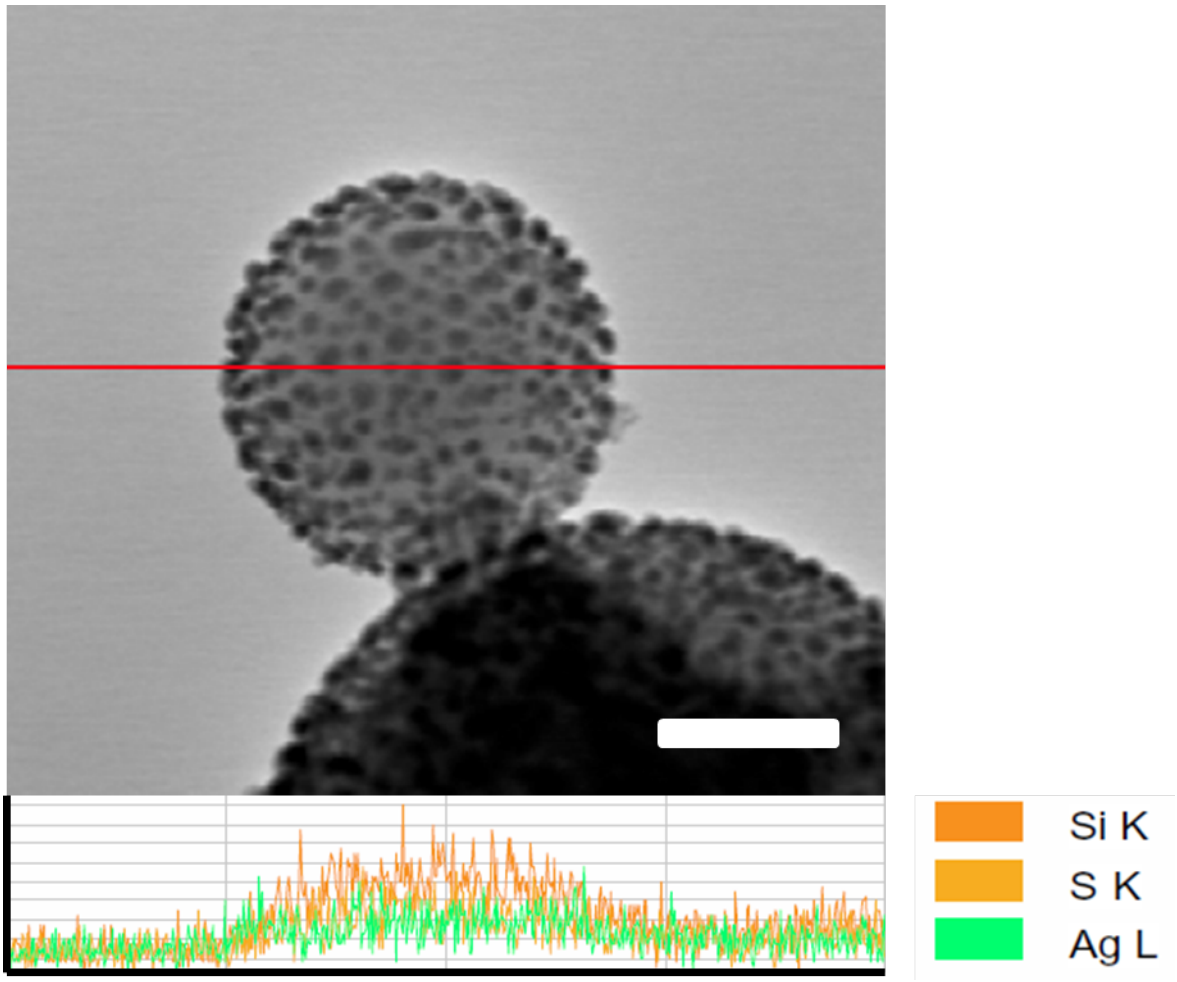


Figure S11: TEM micrograph of surface immobilized SH50 nanoparticles loaded with Ag^0 nanocrystals.

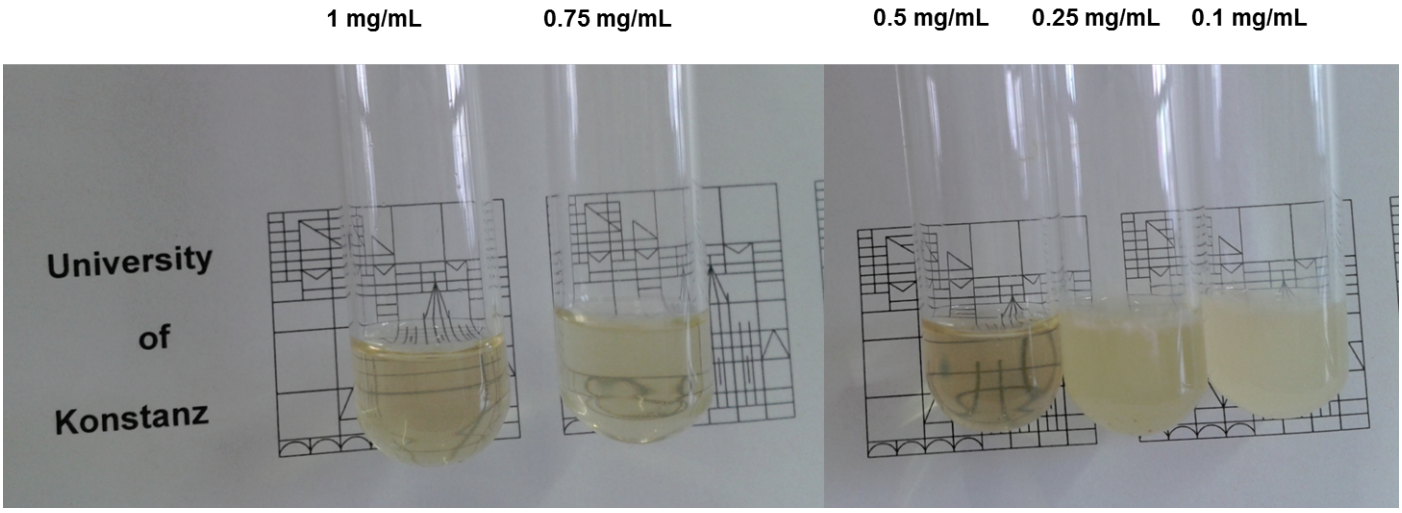


scale bar = 100 nm

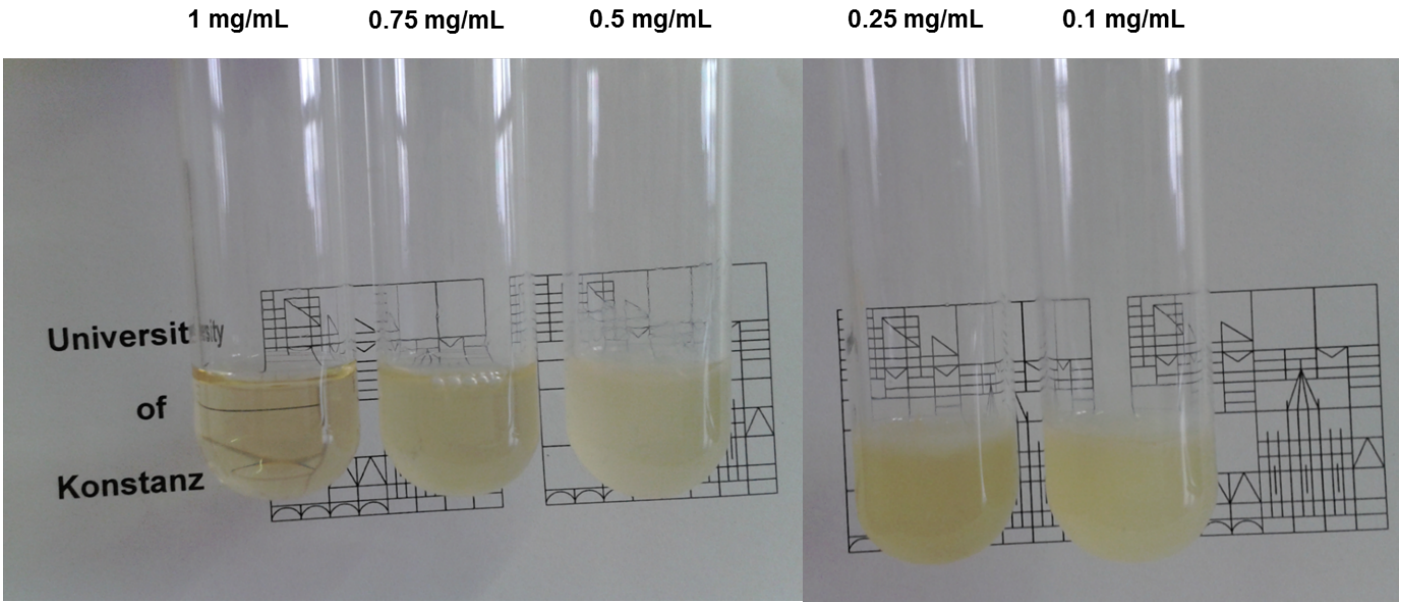
Figure S12: Biological experiments.

Pictures of MIC test

Ag^0@SH50 nanoparticles



Ag^0@SH100 nanoparticle



References Supporting Information:

1. Gehring, J.; Schleheck, D.; Luka, M.; Polarz, S., Aerosol-Synthesis of Mesoporous Organosilica Nanoparticles with Highly Reactive, Superacidic Surfaces Comprising Sulfonic Acid Entities. *Adv. Funct. Mater.* **2014,** *24*, 1140-1150.