

Supporting materials

Mesoporous SnO₂–SiO₂ and Sn–Silica–Carbon nanocomposites by novel non-hydrolytic templated sol-gel synthesis

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GC-MS of byproducts

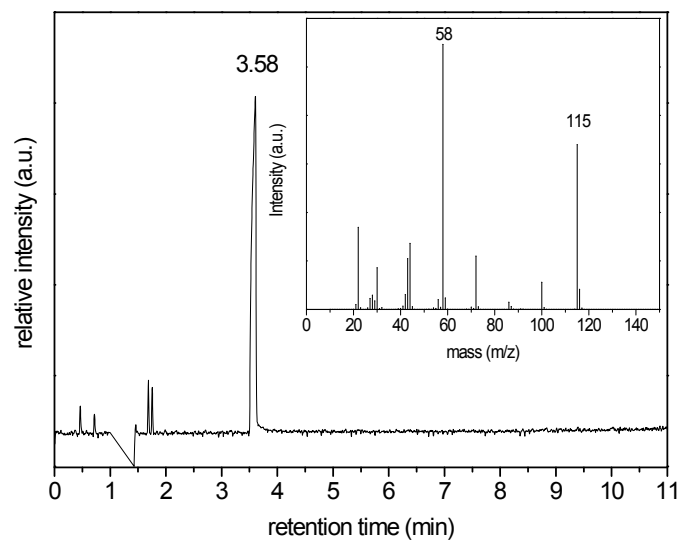


Fig. 1S GC chromatogram and MS spectrum at 3.58 min of $\text{Si}(\text{OAc})_4 + \text{Sn}(\text{NEt}_2)_4$ reaction byproducts.

TG/DSC curves

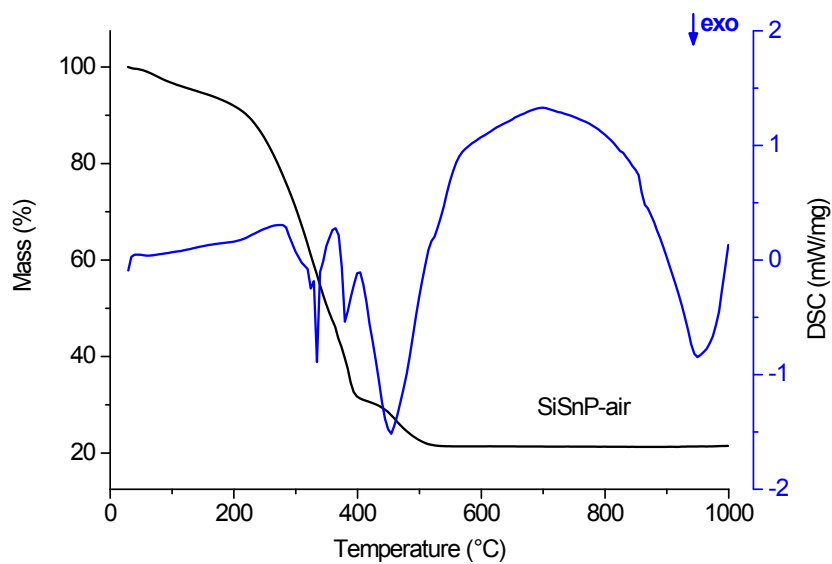


Fig. 2S TG/DSC curves of SiSnP sample. The analysis was performed in air.

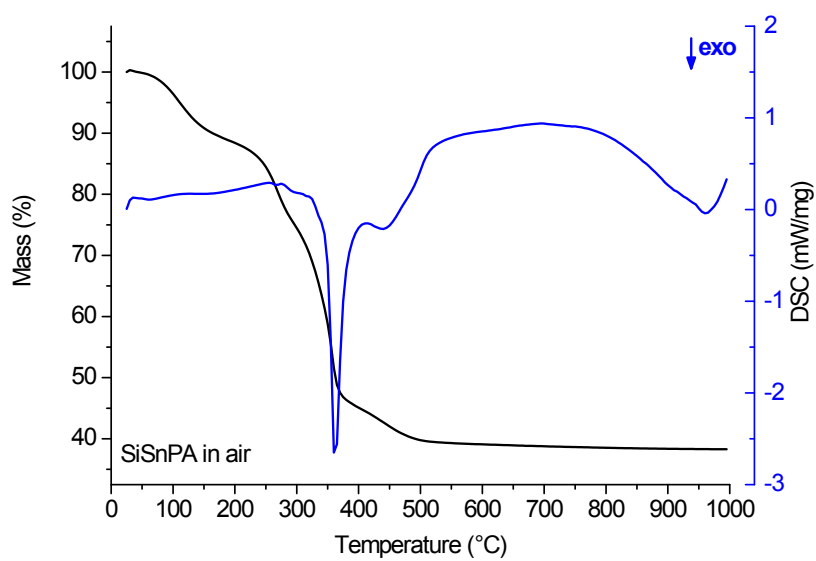


Fig. 3S TG/DSC curves of SiSnPA sample. The analysis was performed in air.

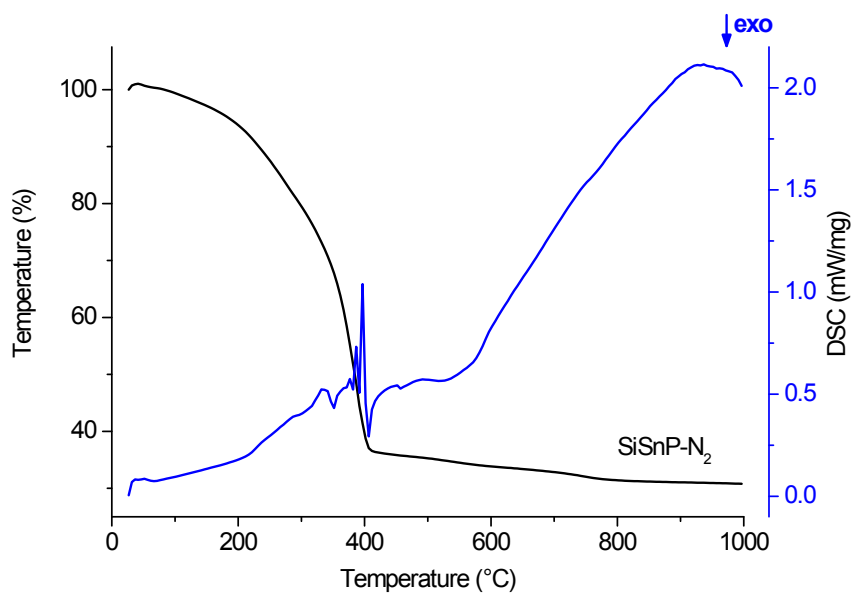


Fig. 4S TG/DSC curves of SiSnP sample. Analyses were performed in N₂.

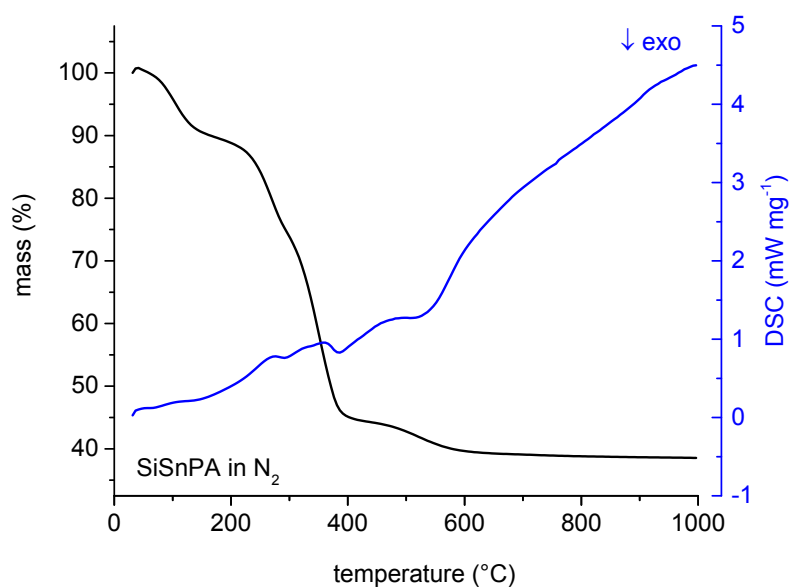


Fig. 55 TG/DSC curves of SiSnPA sample. The analysis was performed in N₂.

HT powder XRD

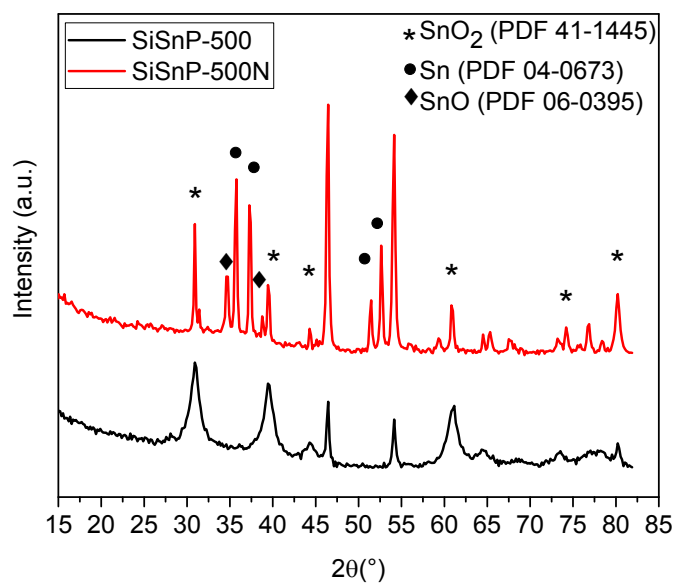


Fig. 65 Powder XRD patterns of SiO₂-SnO₂ nanocomposites SiSnP500 and SiSnP-500N.

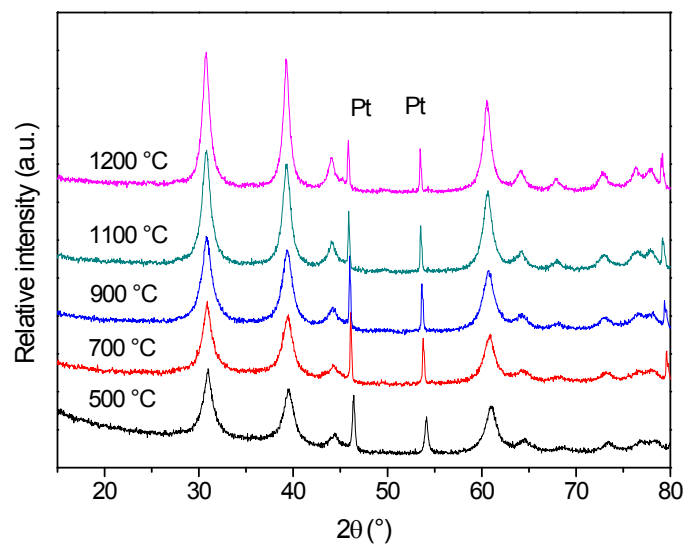


Fig. 7S HT powder XRD patterns of $\text{SiO}_2\text{-SnO}_2$ nanocomposite SiSnP with the diffractions of SnO_2 (PDF 41-1445).

Table 1S Size of SnO_2 nanoparticles determined by the Rietveld refinement in SiSnP sample calcined at different temperatures

Temperature [°C]	Size of the crystallites [nm]			
	1,0,0	0,0,1	1,1,0	1,1,1
500	7.33	6.22	7.33	6.68
600	7.27	6.25	7.27	6.68
700	7.51	6.35	7.51	6.82
800	6.96	6.45	6.96	6.68
900	6.75	7.18	6.75	6.97
1000	7.12	8.60	7.12	7.80
1100	8.34	9.10	8.34	8.86
1200	9.99	12.32	9.99	11.32

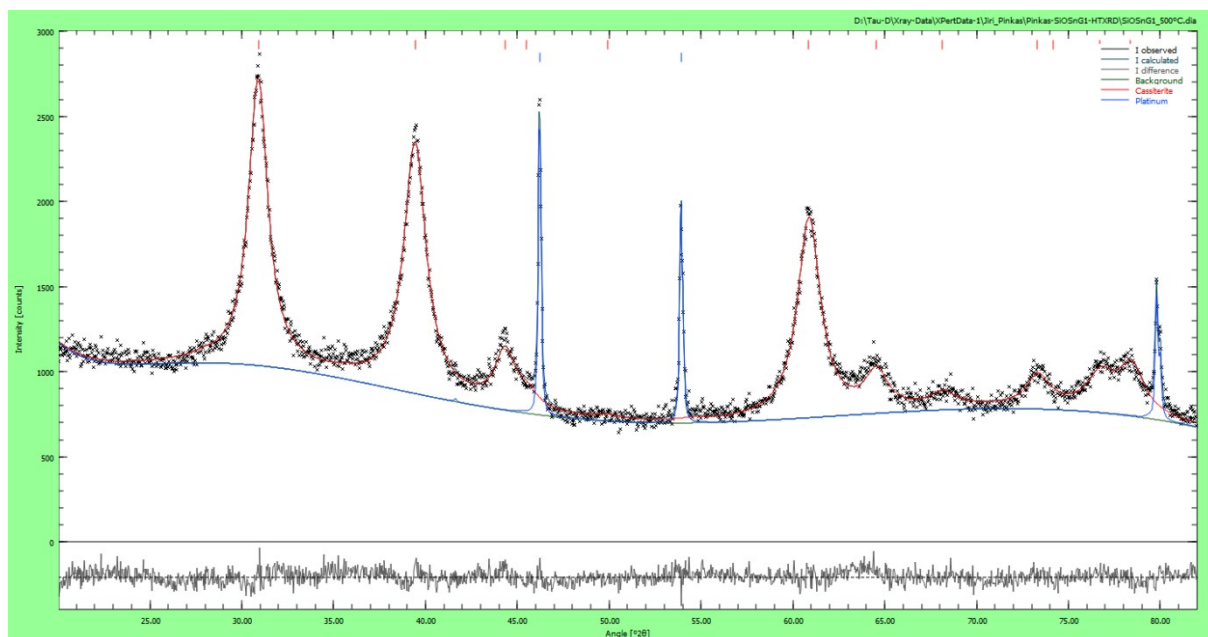


Fig. 8S Rietveld refinement pattern of SiSnP-500.

Rietveld refinement to file(s) SiSnP_500°C.xy

BGMN version 4.2.22, 1855 measured points, 15 peaks, 37 parameters

Rp=3.01% Rpb=14.14% R=3.63% Rwp=3.81% Rexp=3.05%

Durbin-Watson d=1.46

1-rho=1.61%

Global parameters and GOALs

cassiterite/sum=ERROR

P/sum=ERROR

EPS2=0.000795+-0.000038

Local parameters and GOALs for phase Cassiterite

SpacegroupNo=136

HermannMauguin=P4₂/m2₁/n2/m

XrayDensity=6.997

Rphase=3.34%

UNIT=NM

A=0.473419+-0.000067

C=0.319084+-0.000067

GrainSize(1,0,0)=7.335+-0.094

GrainSize(0,0,1)=6.22+-0.11

GrainSize(1,1,0)=7.335+-0.094

GrainSize(1,1,1)=6.682+-0.070

GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.0848214

B1=ANISOLIN, MeanValue(B1)=0.0614393, sqrt3(det(B1))=0.0611355

Atomic positions for phase Cassiterite

2 0.0000 0.0000 0.0000 E=(SN+4(1.0000))

4 0.6947 0.6947 0.0000 E=(O-2(1.0000))

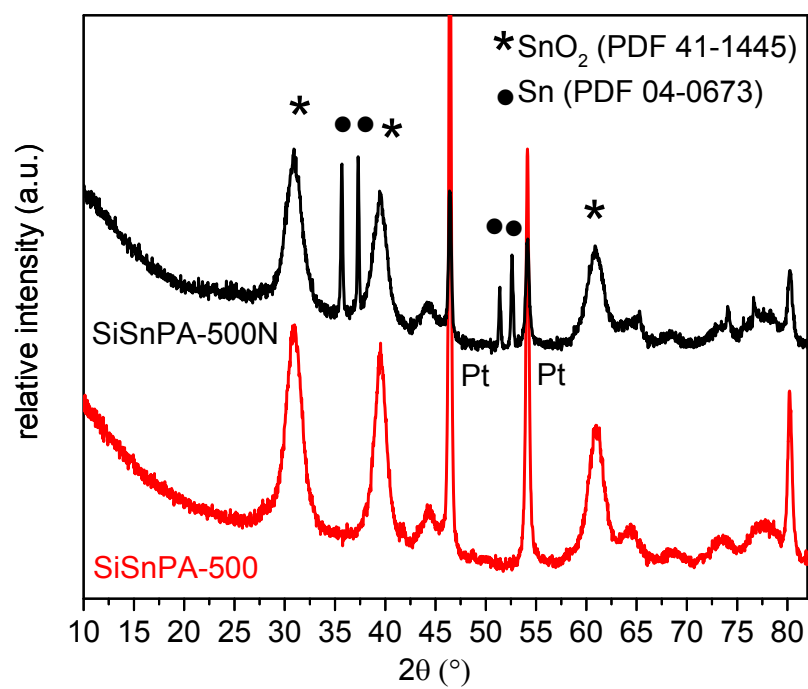


Fig. 9S Powder XRD patterns of SiSnPA-500 and SiSnPA-500N nanocomposites.

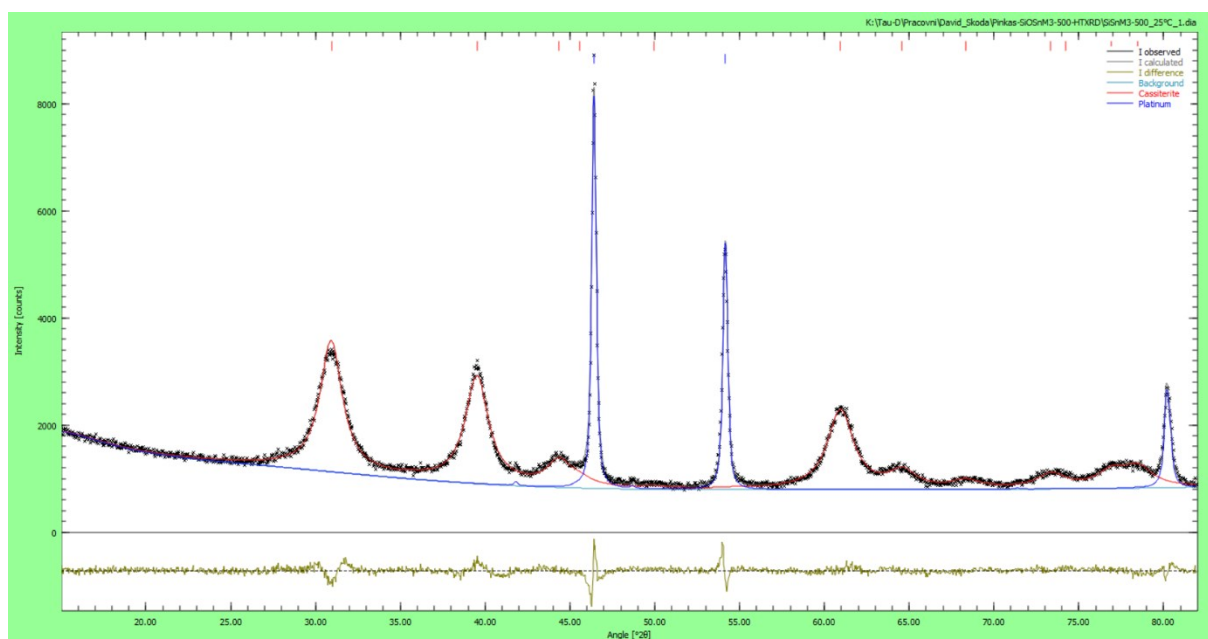


Fig. 10S Rietveld refinement pattern of SiSnPA-500.

Rietveld refinement to file(s) SiSnPA-500.xy

BGMN version 4.2.22, 2005 measured points, 15 peaks, 34 parameters

Rp=3.27% Rpb=11.14% R=4.61% Rwp=4.00% Rexp=2.70%

Durbin-Watson d=0.98

1-rho=0.985%

Global parameters and GOALs

240*EPS2/2=0.0765+-0.0040

EPS2=0.000638+-0.000033

Local parameters and GOALs for phase Cassiterite

SpacegroupNo=136

HermannMauguin=P4₂/m2₁/n2/m

XrayDensity=7.018

Rphase=4.11%

UNIT=NM

A=0.473260+-0.000068

C=0.318366+-0.000067

k2=0.0000069+-0.0000045

B1=0.0721+-0.0011

GrainSize(1,1,1)=5.890+-0.092

my=0.203889+-0.000065

GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.136657

Atomic positions for phase Cassiterite

2 0.0000 0.0000 0.0000 E=(SN+4(1.0000))
4 0.6947 0.6947 0.0000 E=(O-2(1.0000))

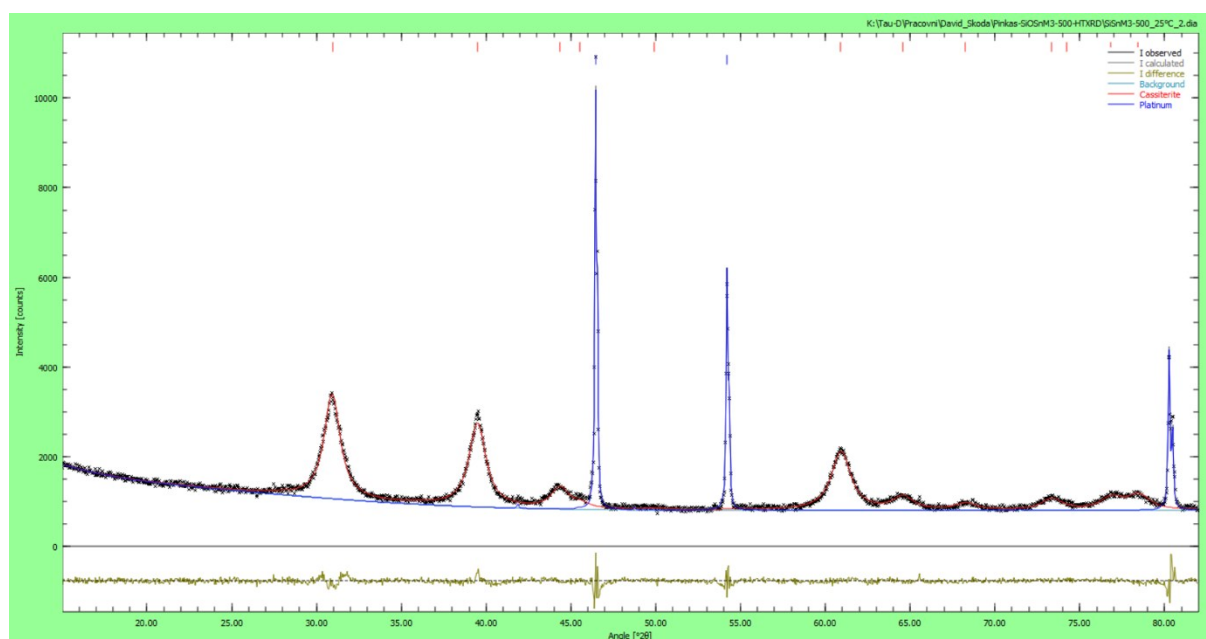


Fig. 11S Rietveld refinement pattern of SiSnP-500 after calcination up to 1200 °C.

Rietveld refinement to file(s) SiSnPA-500_1200°C.xy

BGMN version 4.2.22, 2005 measured points, 15 peaks, 34 parameters

Rp=3.16% Rpb=14.09% R=4.62% Rwp=3.93% Rexp=2.87%

Durbin-Watson d=1.36

1-rho=1.12%

Global parameters and GOALs

240*EPS2/2=0.0594+-0.0017

EPS2=0.000495+-0.000014

Local parameters and GOALs for phase Cassiterite

SpacegroupNo=136

HermannMauguin=P4₂/m2₁/n2/m

XrayDensity=7.004

Rphase=3.74%

UNIT=NM

A=0.473489+-0.000049

C=0.318699+-0.000052

k2=0.0000080+-0.0000031

B1=0.05079+-0.00085

GrainSize(1,1,1)=8.36+-0.14

my=0.203478+-0.000043

GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.0933681

Atomic positions for phase Cassiterite

2 0.0000 0.0000 0.0000 E=(SN+4(1.0000))
4 0.6947 0.6947 0.0000 E=(O-2(1.0000))

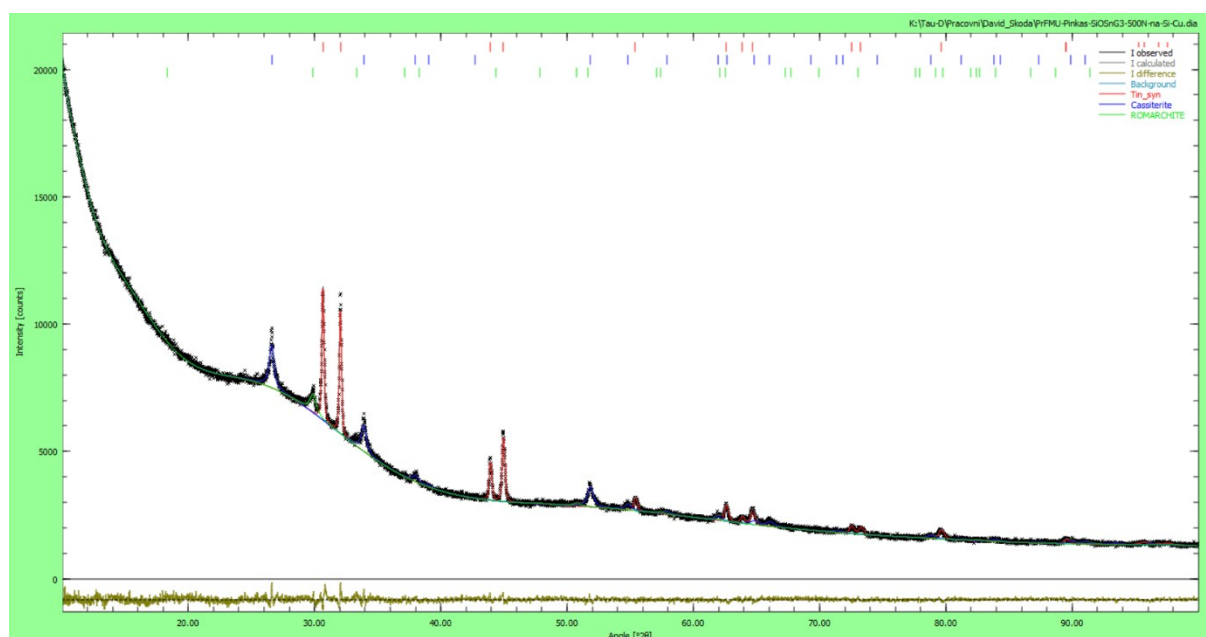


Fig. 12S Rietveld refinement pattern of SiSnF-500N.

Rietveld refinement to file(s) SiOSnF-500N.xy

BGMN version 4.2.22, 6854 measured points, 77 peaks, 70 parameters

Rp=1.38% Rpb=39.71% R=1.47% Rwp=1.88% Rexp=1.53%

Durbin-Watson d=1.31

1-rho=0.160%

Global parameters and GOALs

tin/sum=0.5587+-0.0047

cassiterite/sum=0.3794+-0.0049

romarchite/sum=0.0618+-0.0051

240*EPS2/2=ERROR

Local parameters and GOALs for phase Tin_syn

SpacegroupNo=141

HermannMauguin=I4₁/a2/m2/d

XrayDensity=7.309

Rphase=2.94%

UNIT=NM

A=0.582520+-0.000013

C=0.317844+-0.000010

k2=0.00000505+-0.00000043

B1=0.00291+-0.00024

GrainSize(1,1,1)=146+-12

my=0.1805331+-0.0000079

GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.0296591

Atomic positions for phase Tin_syn

4 0.0000 0.0000 0.0000 E=(SN(1.0000))

Local parameters and GOALs for phase Cassiterite

SpacegroupNo=136

HermannMauguin=P4₂/m2₁/n2/m

XrayDensity=7.018

Rphase=2.48%

UNIT=NM

A=0.473275+-0.000046

C=0.318318+-0.000058

k2=0.0000022+-0.0000013

B1=0.02112+-0.00083

GrainSize(1,1,1)=20.09+-0.79

my=0.138258+-0.000027

GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.0207914

Atomic positions for phase Cassiterite

2 0.0000 0.0000 0.0000 E=(SN+4(1.0000))

4 0.6947 0.6947 0.0000 E=(O-2(1.0000))

Local parameters and GOALs for phase ROMARCHITE

SpacegroupNo=129
 HermannMauguin=P4/n2₁/m2/m
 XrayDensity=6.408
 Rphase=2.12%
 UNIT=NM
 k2=0
 B1=0.0300000
 GrainSize(1,1,1)=14.1471
 my=0.140348
 GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.00338229
 Atomic positions for phase ROMARCHITE

```

2  0.0000 0.0000 0.0000  E=(O-2(1.0000))
2  0.0000 0.5000 0.2345  E=(SN+2(1.0000))
  
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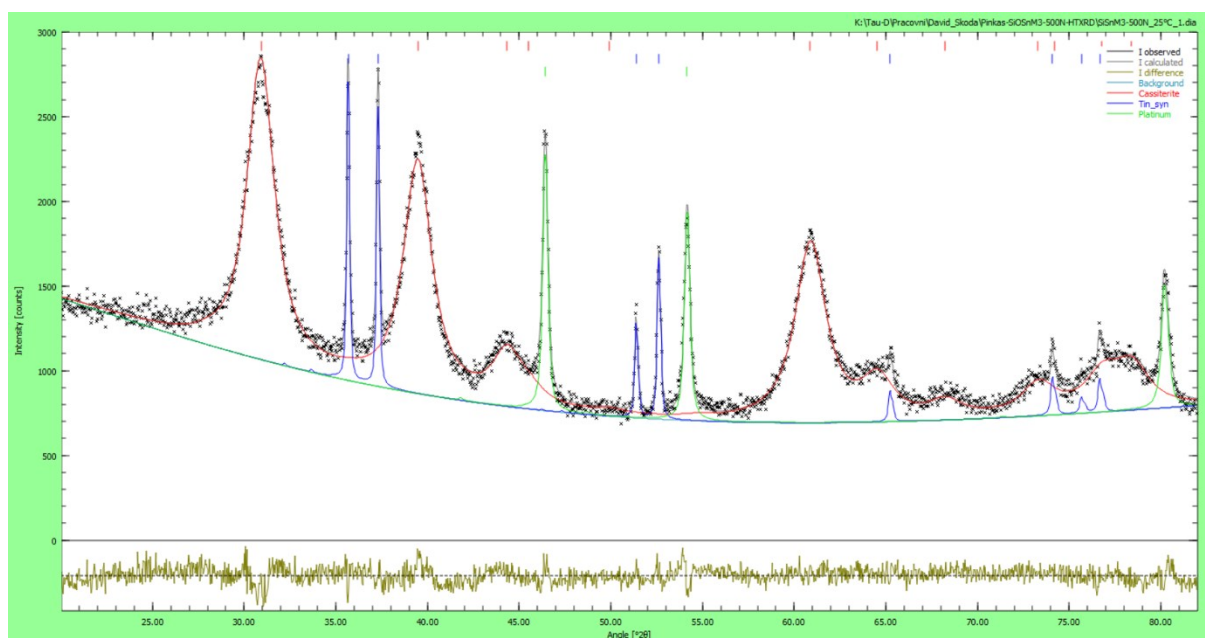


Fig. 13S Rietveld refinement pattern of SiSnPA-500N.

Rietveld refinement to file(s) SiSnPA-500N.xy

Rp=3.16% Rpb=11.84% R=3.81% Rwp=3.92% Rexp=2.89%
 Durbin-Watson d=1.25
 1-rho=1.49%

Global parameters and GOALs

cassiterite/sum=0.9036+-0.0018
 tin/sum=0.0964+-0.0018
 240*EPS2/2=0.0653+-0.0044
 EPS2=0.000544+-0.000037

Local parameters and GOALs for phase Cassiterite

SpacegroupNo=136

HermannMauguin=P4_2/m2_1/n2/m
 XrayDensity=6.997
 Rphase=3.65%
 UNIT=NM
 A=0.473588+-0.000082
 C=0.318865+-0.000082
 k2=0
 B1=0.0726+-0.0030
 k1=0.177+-0.087
 GrainSize(1,1,1)=5.333+-0.057
 my=0.203287+-0.000076
 GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.101946
 Atomic positions for phase Cassiterite

```

-----
 2  0.0000 0.0000 0.0000  E=(SN+4(1.0000))
 4  0.6947 0.6947 0.0000  E=(O-2(1.0000))
  
```

Local parameters and GOALs for phase Tin_syn

SpacegroupNo=141
 HermannMauguin=I4_1/a2/m2/d
 XrayDensity=7.291
 Rphase=3.81%
 UNIT=NM
 A=0.582993+-0.000057
 C=0.318117+-0.000034
 k2=0.00000063+-0.00000034
 B1=0.00395+-0.00037
 GrainSize(1,1,1)=107+-10
 my=0.265389+-0.000073
 GEWICHT=SPHAR4, MeanValue(GEWICHT)=0.0103778
 Atomic positions for phase Tin_syn

```

-----
 4  0.0000 0.0000 0.0000  E=(SN(1.0000))
  
```

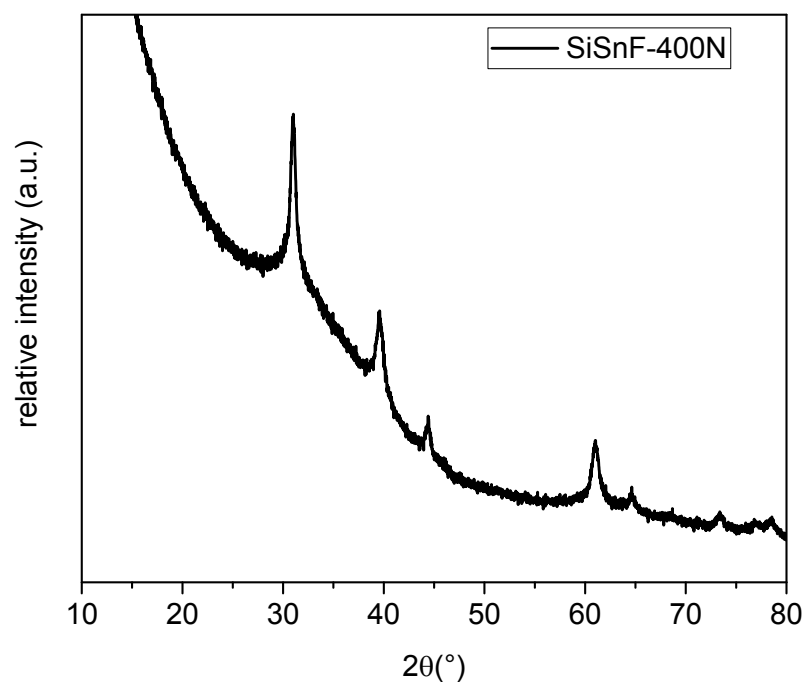


Fig. 14S Powder XRD diffractogram of the sample SiSnF-400N. The diffractions correspond to SnO_2 (PDF 41-1445).

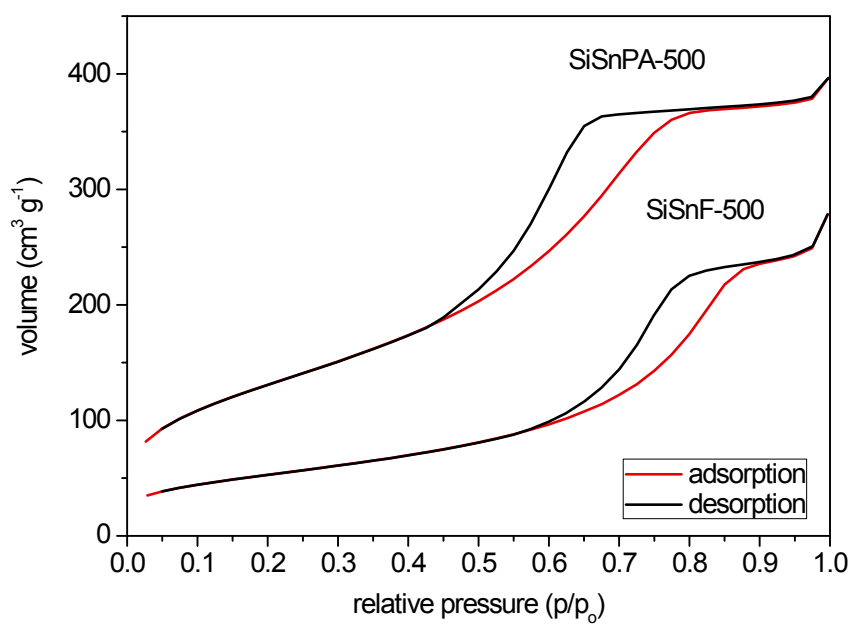


Fig. 15S N_2 adsorption/desorption isotherms of air calcined xerogels. SiSnPA-500 sample (top) prepared in an autoclave, SiSnF-500 (bottom) prepared with the Schlenk technique.

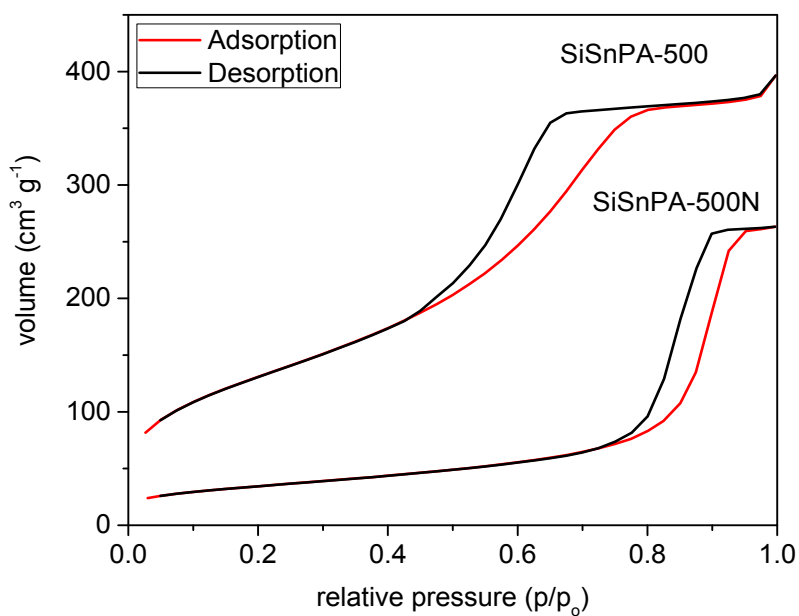


Fig. 16S N_2 adsorption/desorption isotherms of air calcined xerogels. SiSnPA-500 sample (top) calcined in air and SiSnPA-500N sample heated under N_2 .

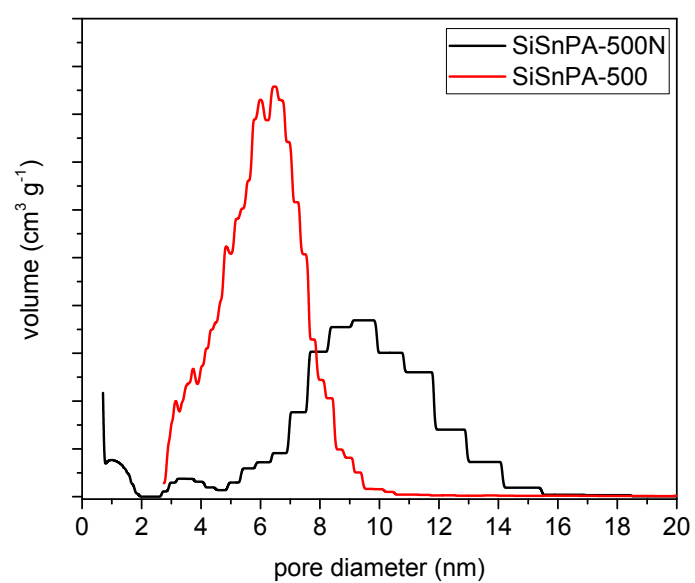


Fig. 17S Pore size distributions based on NLDFT (adsorption branch) (red) and QSDFT (black) models.

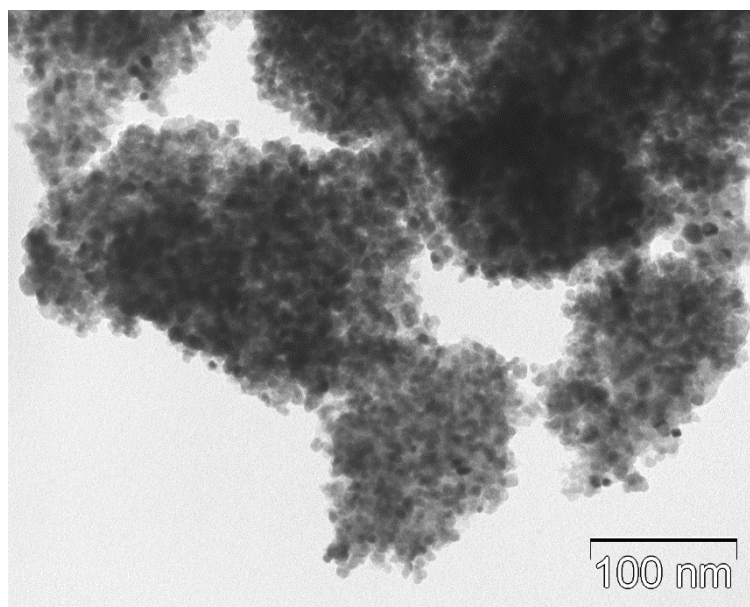


Fig. 18S TEM image of SiSnPA-500 xerogel.

Pyridine adsorption

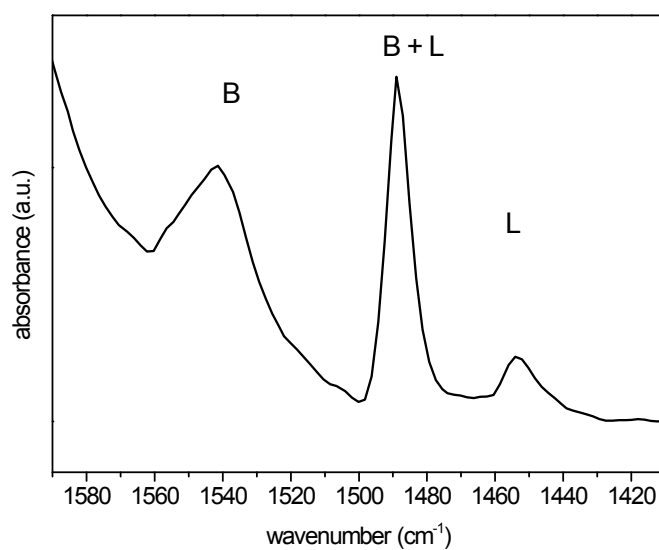


Fig. 19S IR spectrum of calcined SiSnP-500 xerogel after pyridine adsorption.

Catalysis

Aminolysis of styrene oxide

Conditions: 25 mg of calcined $\text{SnO}_2\text{-SiO}_2$ xerogel, 5 mmol of substrates, 5 cm^3 of toluene, 50 °C.

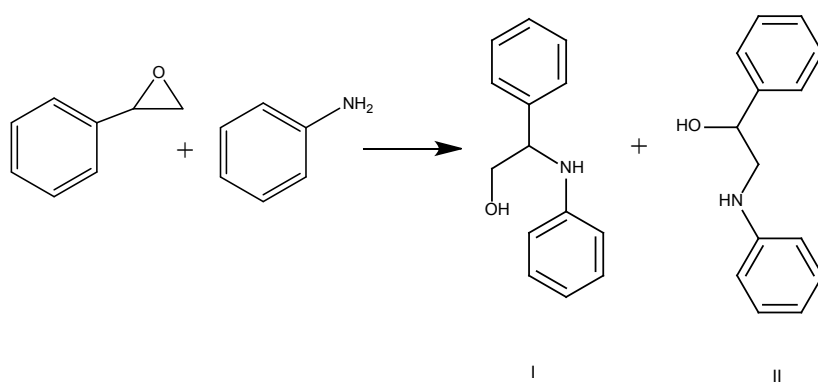


Fig. 20S Aminolysis of styrene oxide with aniline.

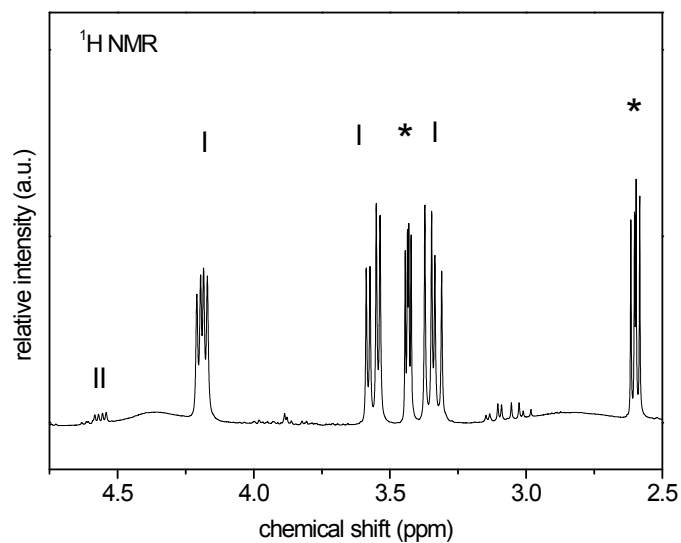


Fig. 21S ¹H NMR spectrum of a reaction mixture after aminolysis reaction.

MPV reduction of 4-*tert*-butylcyclohexanone

Conditions: 25 mg of calcined SnO₂-SiO₂ xerogel, 500 mg (3.54 mmol) of 4-*tert*-butylcyclohexanone, 15 cm³ (196 mmol) of dry 2-propanol, and 0.100 cm³ of nonane as an internal standard. Reaction mixture was refluxed for 1 h.

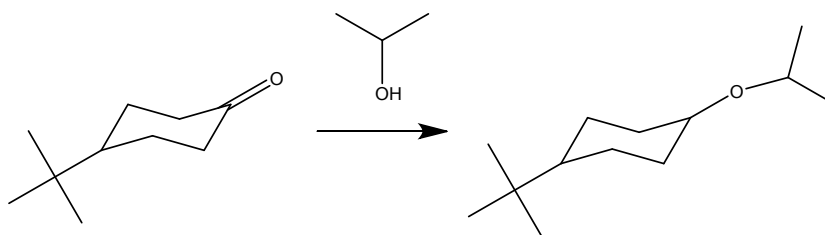


Fig. 22S MPV reduction of 4-*tert*-butylcyclohexanone in isopropanol.

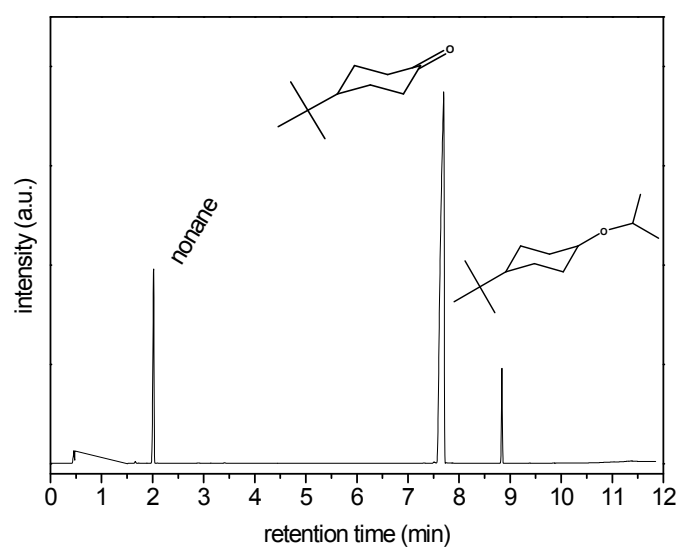


Fig. 235 GC chromatogram of reaction products in the MPV reduction.