Supporting information

RhNPs supported in N-functionalized mesoporous silica: effect on catalyst stabilization and catalytic activity

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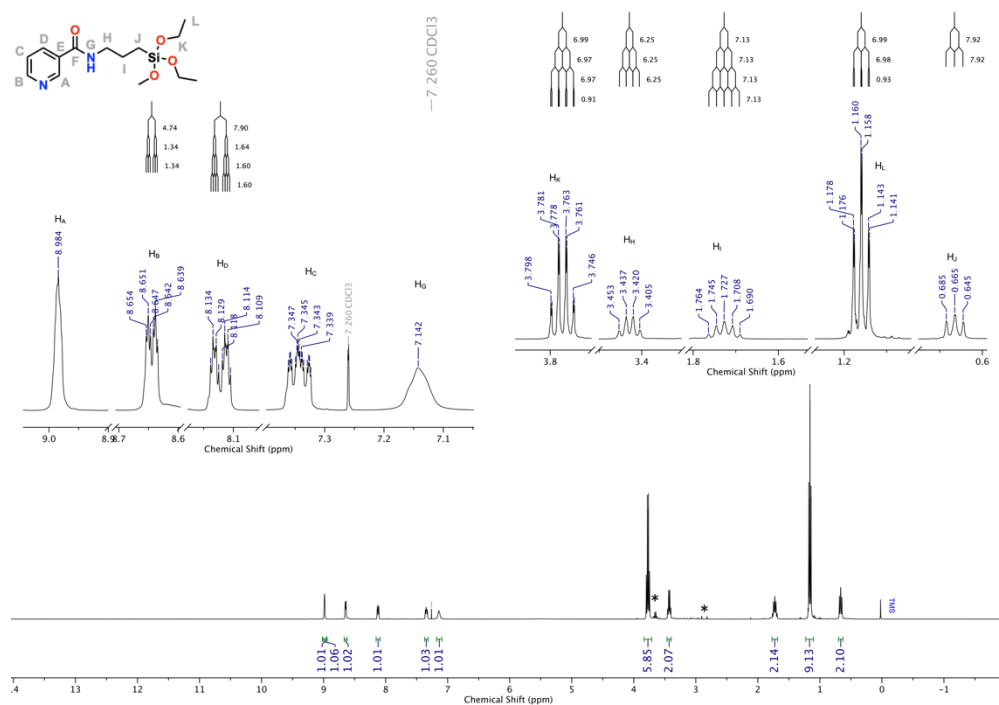
1. NMR spectra of (EtO)₃Si-(CH₂)₃-NAM

Figure S1 ¹H-NMR spectra (400.13 MHz, r. t., CDCl₃) of N-(3-(triethoxysilyl)propyl) nicotinamide (**NAM**) (*) denotes residual triethylamine on sample.
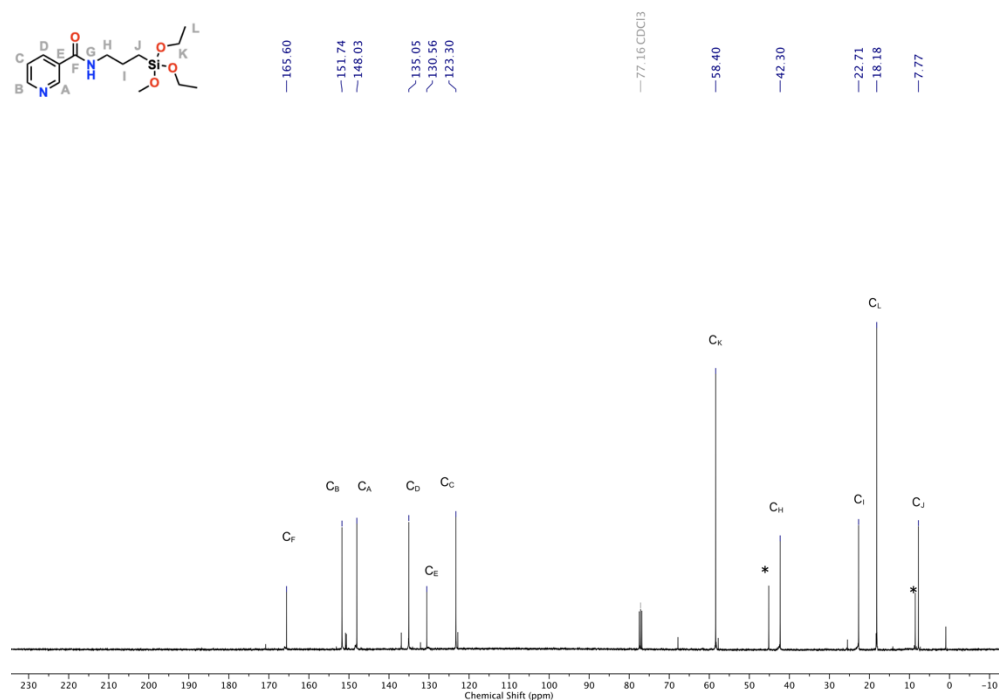

Figure S2 ¹³C{¹H}-NMR spectra (100.61 MHz, r. t., CDCl₃) of **NAM**. Asterisks (*) denotes residual triethylamine on sample.
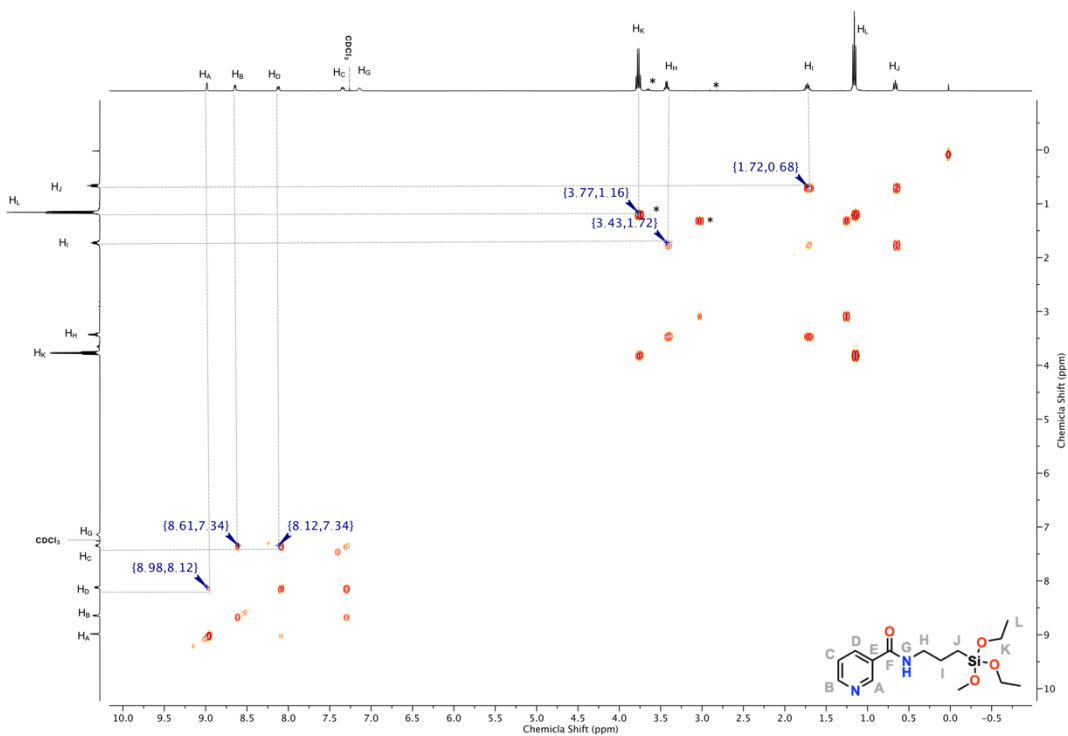
Figure S3 {^{1}H} COSY-NMR spectra (400.13 MHz, r. t., CDCl$_3$) of **NAM** Asterisks (*) denotes residual triethylamine on sample.
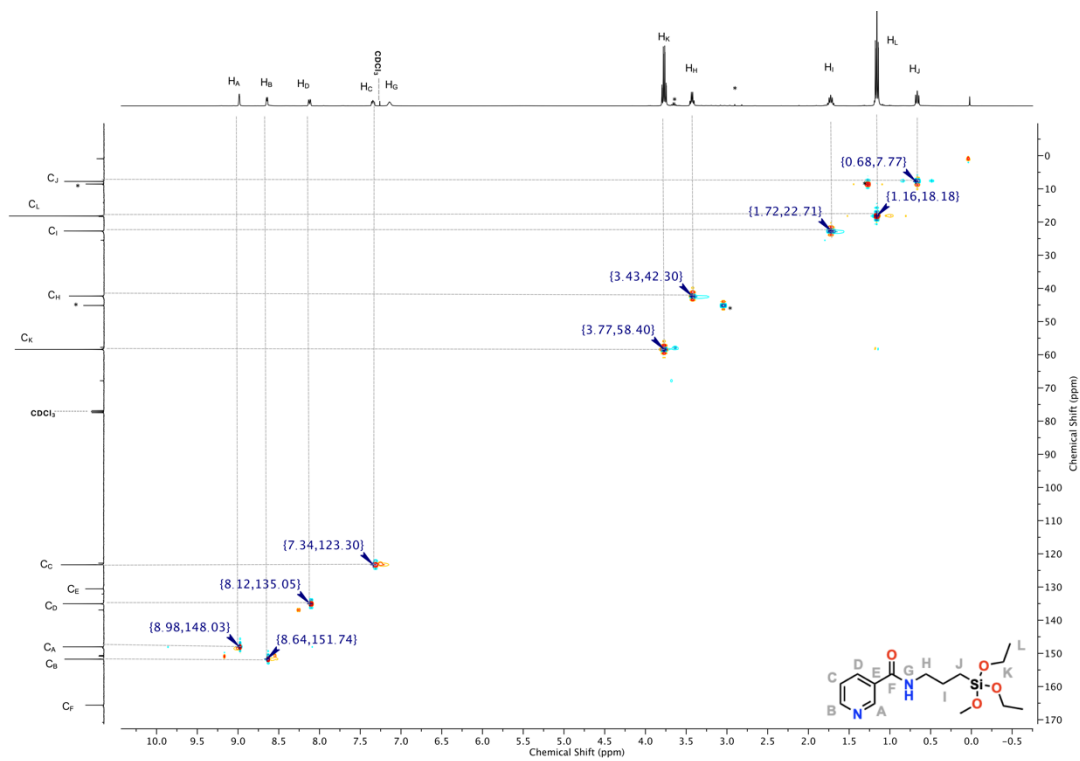

Figure S4 {^{1}H-^{13}C} HSQC-NMR spectra (400.13 MHz, r. t., CDCl$_3$) of **NAM**. Asterisks (*) denotes residual triethylamine on sample

S3

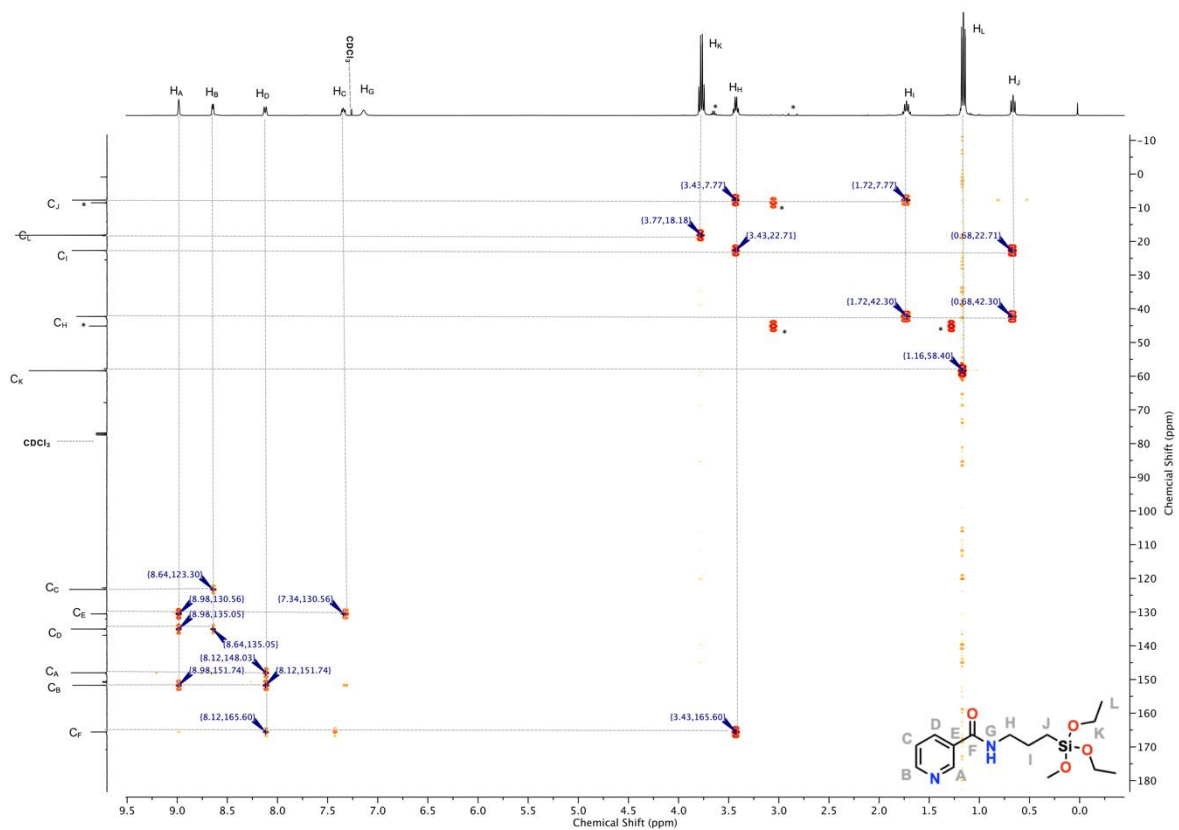**Figure S5** {^{1}H-^{13}C} HMBC-NMR spectra (400.13 MHz, r. t., CDCl$_3$) of **NAM**. Asterisks (*) denotes residual triethylamine on sample.
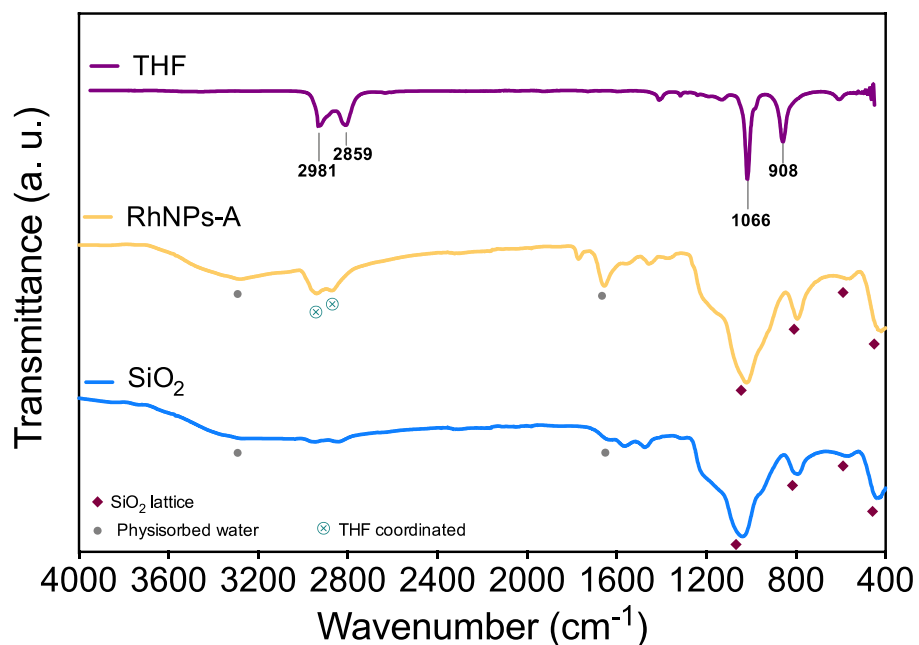
2. FT-IR spectra of supported RhNPs.

Figure S6- IR spectra of SiO$_2$, **RhNPs-A** and THF.

Table S1 Characteristic absorption bands ν (cm^{-1}) in IR spectra of N-grafted silicas and supported RhNPs.

Assignment	SiO$_2$	RhNPs-A	SiO$_2$-APTES	RhNPs-B	SiO$_2$-NAM	RhNPs-C
ν (SiO-H) and ν (HO-H)$_{Phys.}$	3275br 1642w	3277br 1655w	3295br 1635w	3273br 1652m	3298br ----	3296br ---
ν (Si-O-Si)	1039s 947sh 788m	1012s 932sh 791m	1047s 965sh 795m	1043s 961sh 793m	1046s 959sh 795m	1051s 957sh 809m
δ (Si-O)	430m	410m	443m	431m	433m	445m
ν (C-H)	---	---	2923m 2853m	2924m 2854m	2919m 2841m	2926m 2861m
ν (C-N)$_{amine}$	---	---	1219sh	1215sh	---	---
ν (N-H)	---	---	1477w	1465w	1475m	1463m
δ (N-H)	---	---	1555w	1561w	1546m	1541m
γ(N-H) $_{wagg}$	---	---	698vw	---	703vw	699vw
ν(C=O)	---	---	---	---	1640s	1648s
ν_{py} (C=C)	---	---	---	---	1193m	1209m
ν_{py} (C-H)	---	---	---	---	3078w	3091w
ν_{py} (C=N)	---	---	----	-----	1427m	1417m

s (strong), br (broad), m (medium), w (weak), vw (very weak), sh (shoulder), py (pyridine)
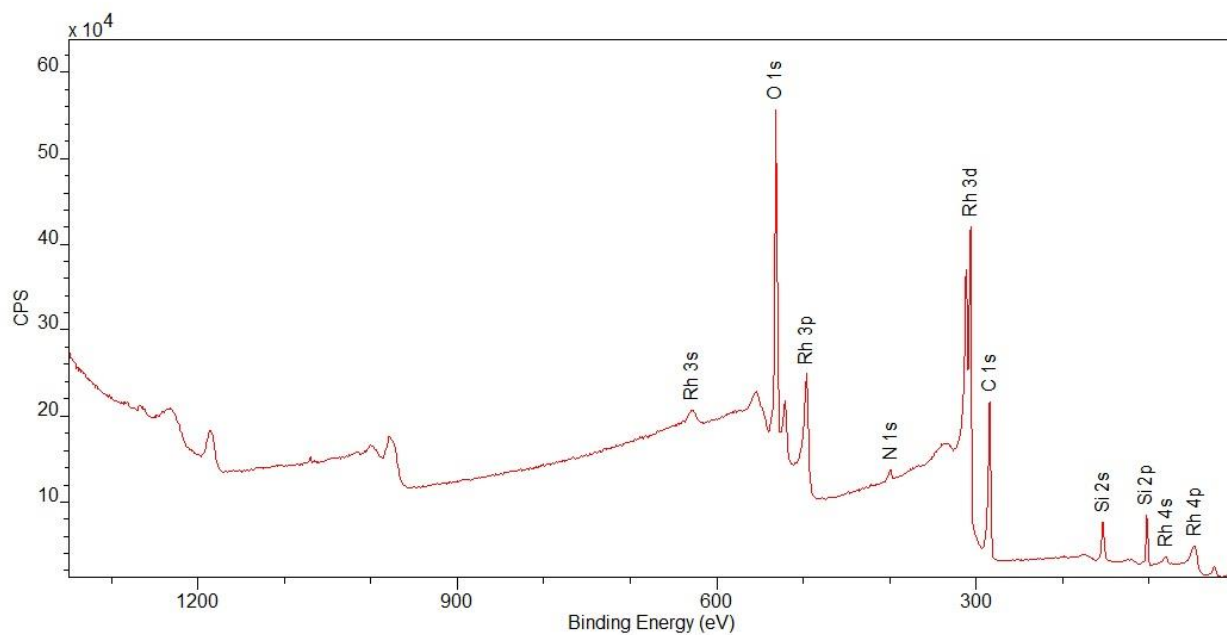
3. XPS analysis of RhNPs

Figure S7 XPS survey of **RhNPs-B**.

Table S2 Element distribution on surface of **RhNPs-B** by XPS.

Element	Atomic %	Weight %
C 1s	40.3	19.8
N 1s	1.5	0.8
O 1s	36.7	24.1
Si 2p	11.5	13.2
Rh 3d	10.0	42.1
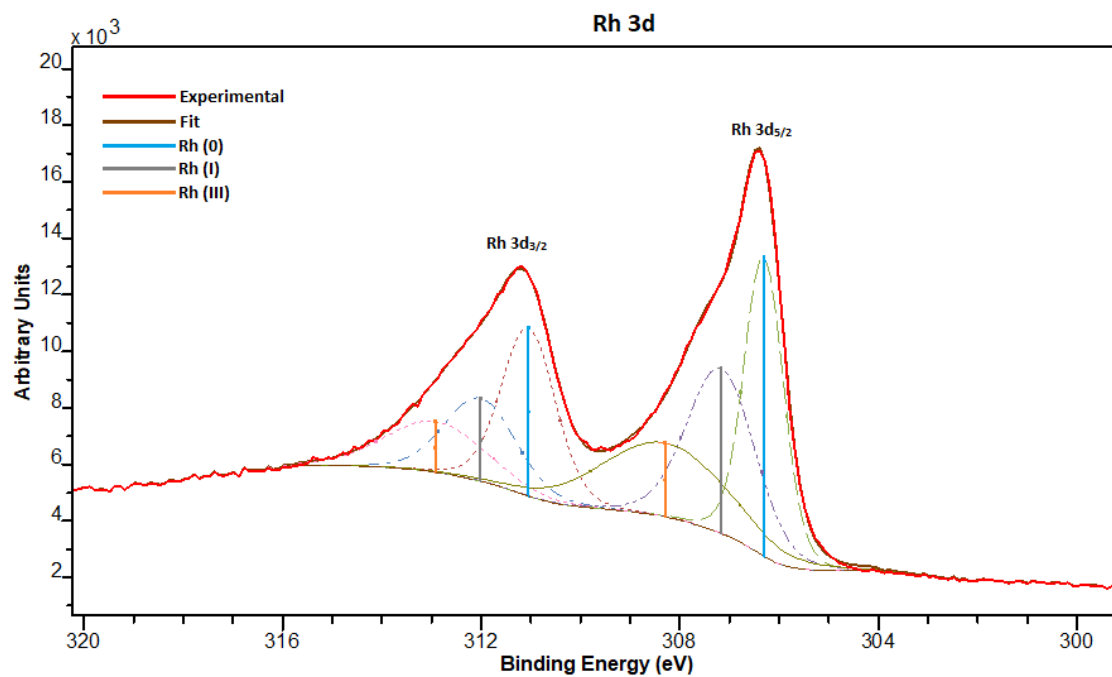
Figure S8 High resolution-XPS Rh 3d of **RhNPs-B**.

Table S3 Rhodium species distribution on surface of **RhNPs-B** by XPS.

	Rh 3d (BE, eV)		Area %
	3/2	5/2	(3d$_{5/2}$)
Rh (0)	311.05	306.31	36.4
Rh (I)	312.01	307.17	34.7
Rh (III)	312.93	308.29	28.9

Residual STD = 1.07199
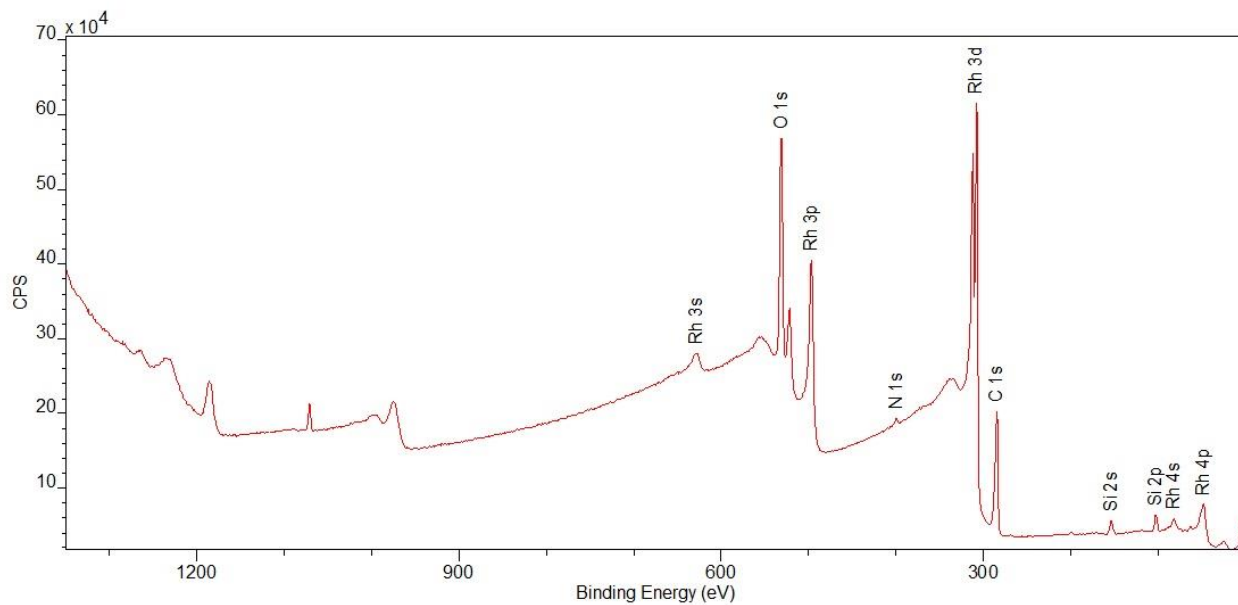
Figure S9 XPS survey of **RhNPs-C.**

Table S4 Element distribution on surface of **RhNPs-C** by XPS.

Element	Atomic %	Weight %
C 1s	39.0	16.1
N 1s	0.9	0.5
O 1s	40.6	22.5
Si 2p	5.6	5.1
Rh 3d	13.9	55.8

4. Thermal decomposition data of synthesized materials
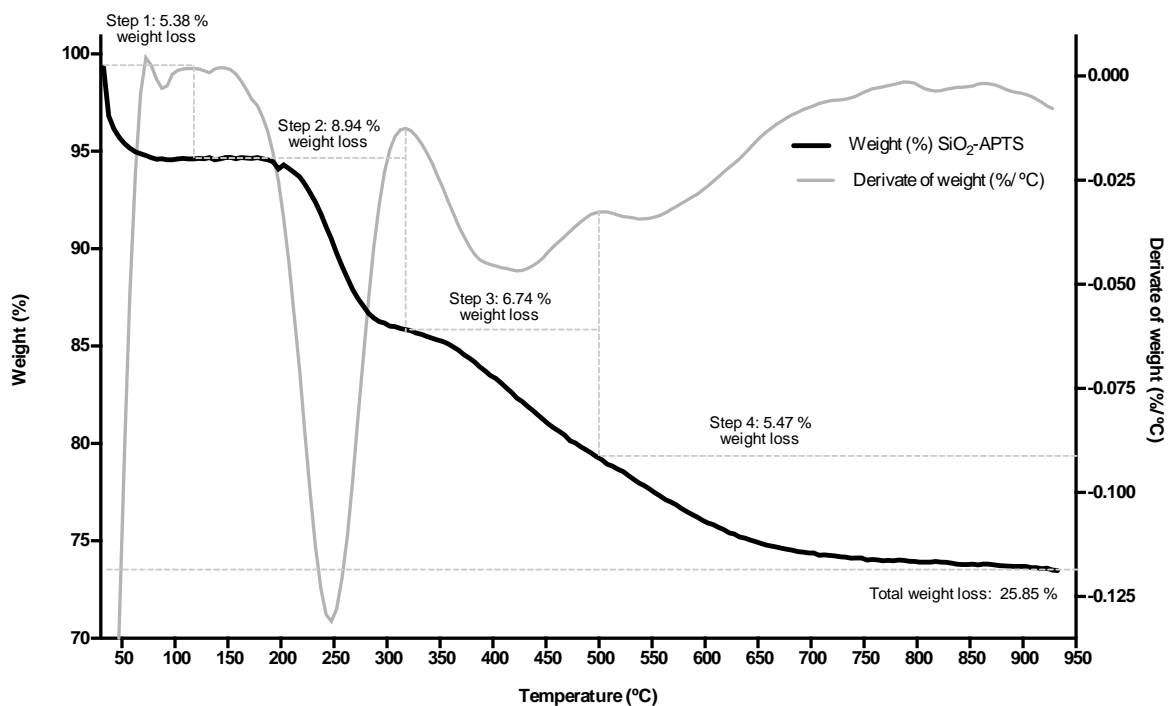
Figure S10 Thermal decomposition data of **SiO₂-APTES** run in air at heating rate of 1 ºC/min.
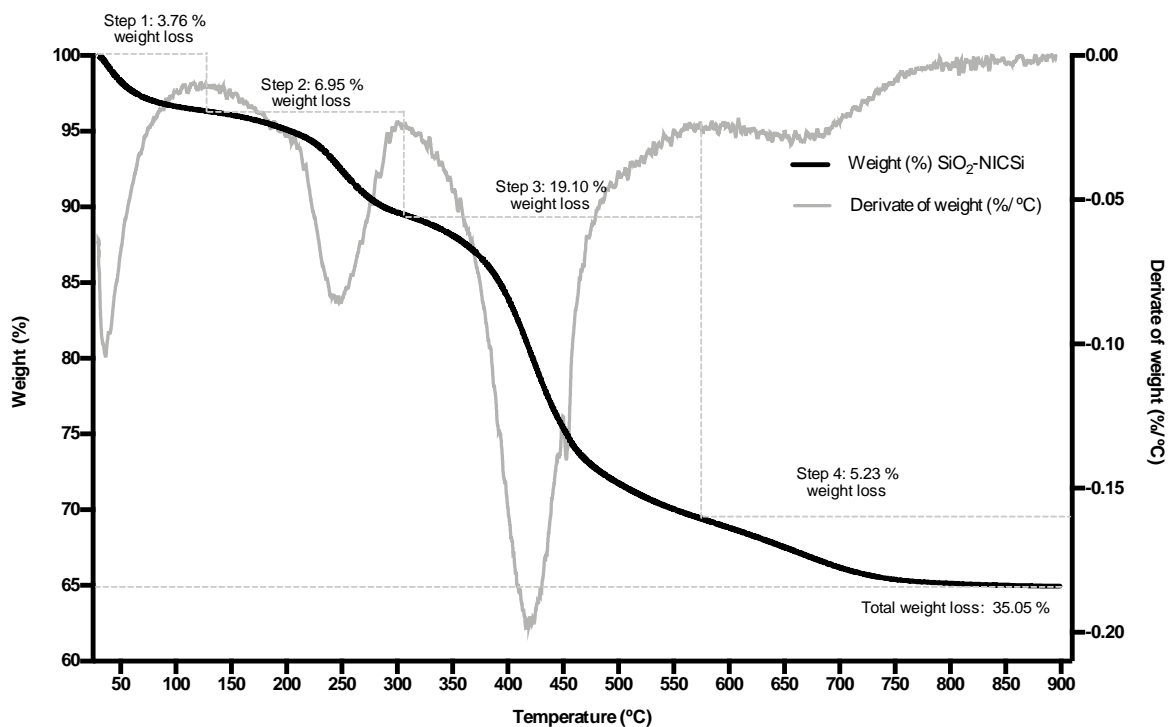
Figure S11 Thermal decomposition data of **SiO₂-(CH₂)₃-NAM** run in air at heating rate of 5 ºC/min.
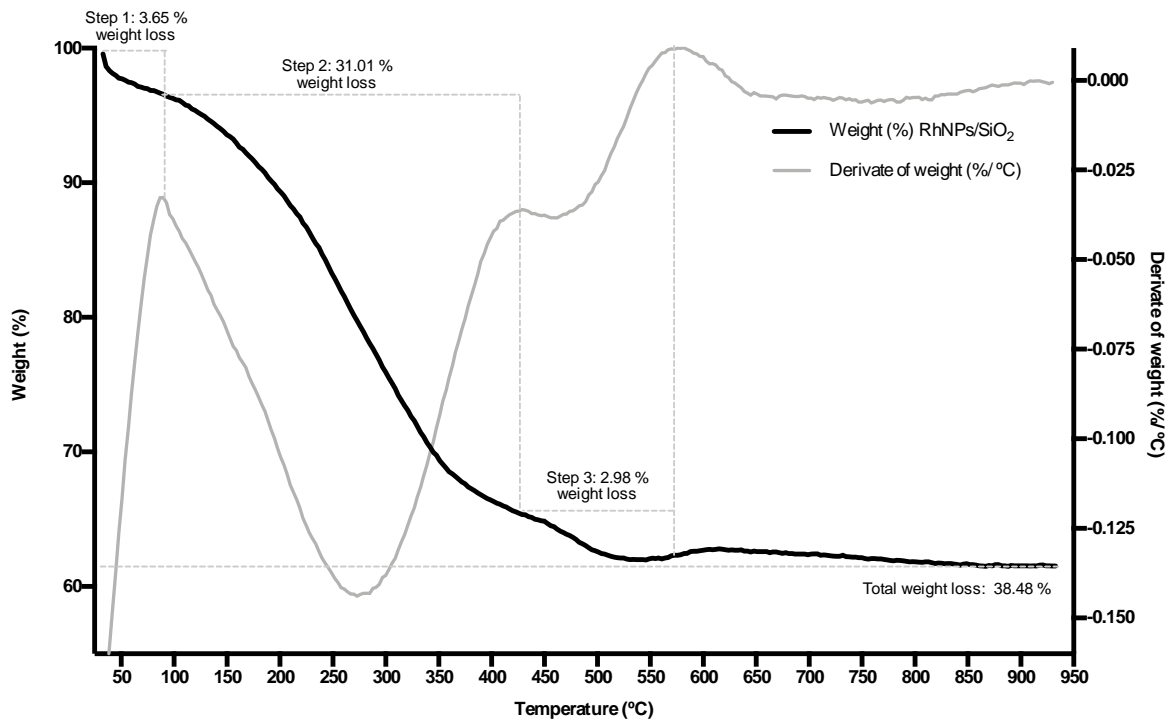
Figure S12 Thermal decomposition data of **RhNPs-A** run in air at a heating rate of 1 °C/min.
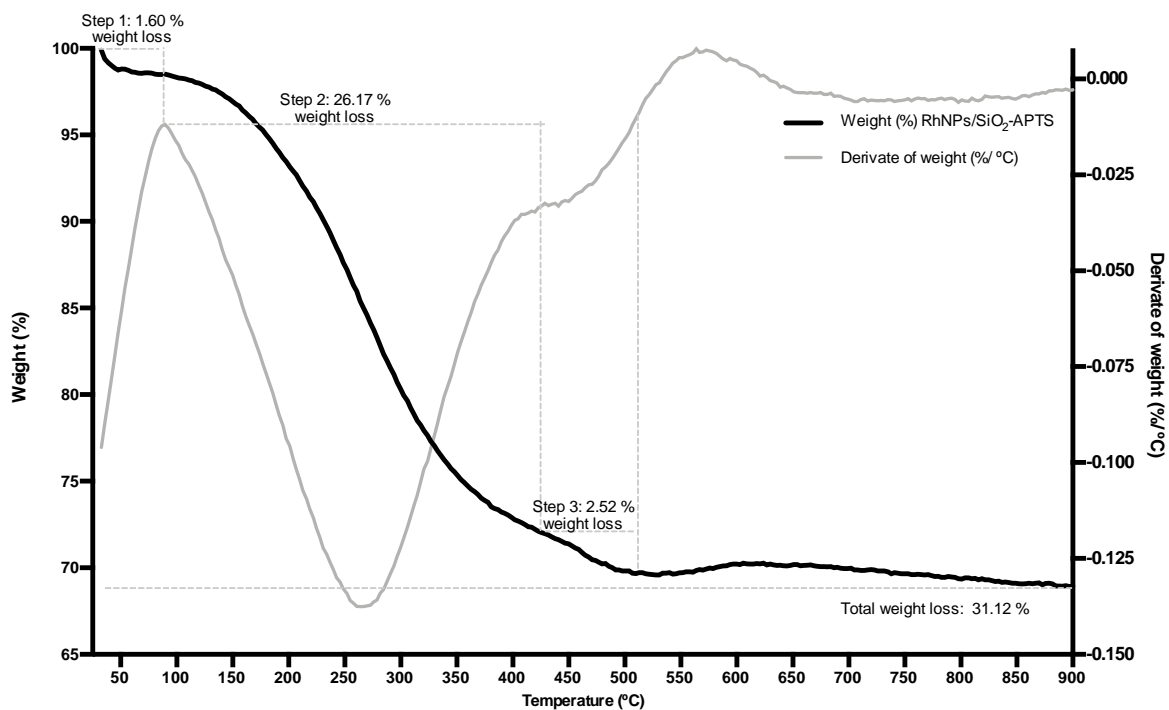
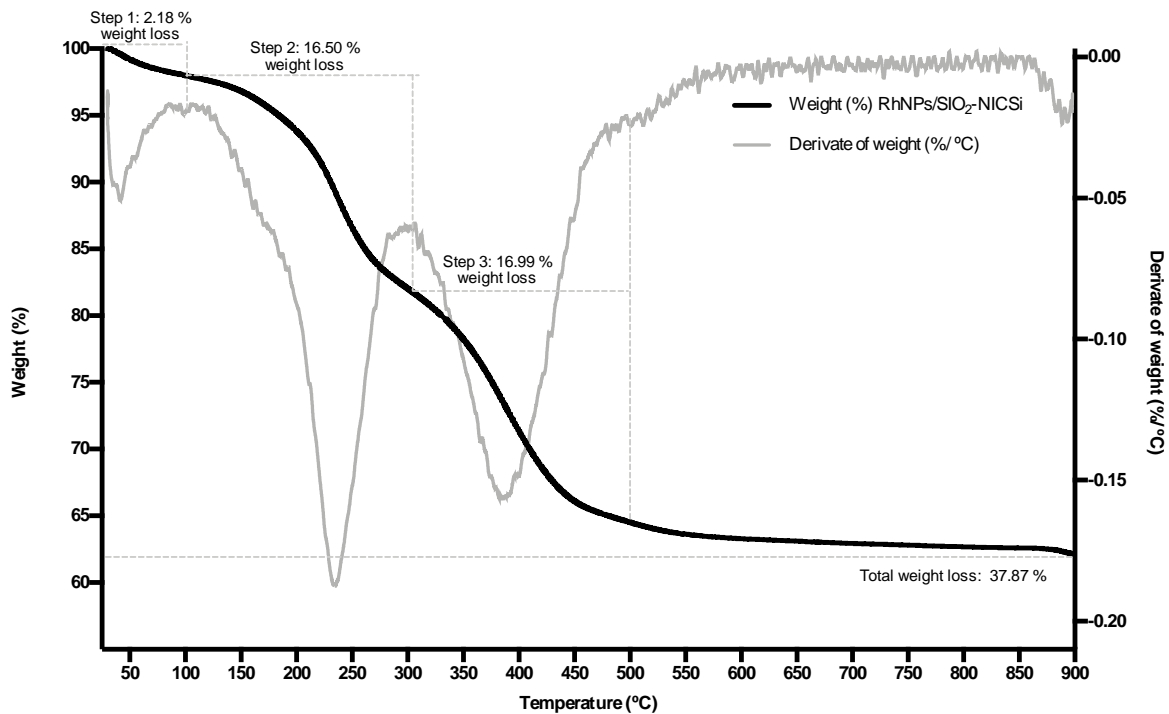**Figure S13** Thermal decomposition data of **RhNPs-B** run in air at a heating rate of 1 °C/min.

Figure S14 Thermal decomposition data of **RhNPs-C** run in air at heating rate of 5 ºC/min.

5. SEM images and particle distribution.
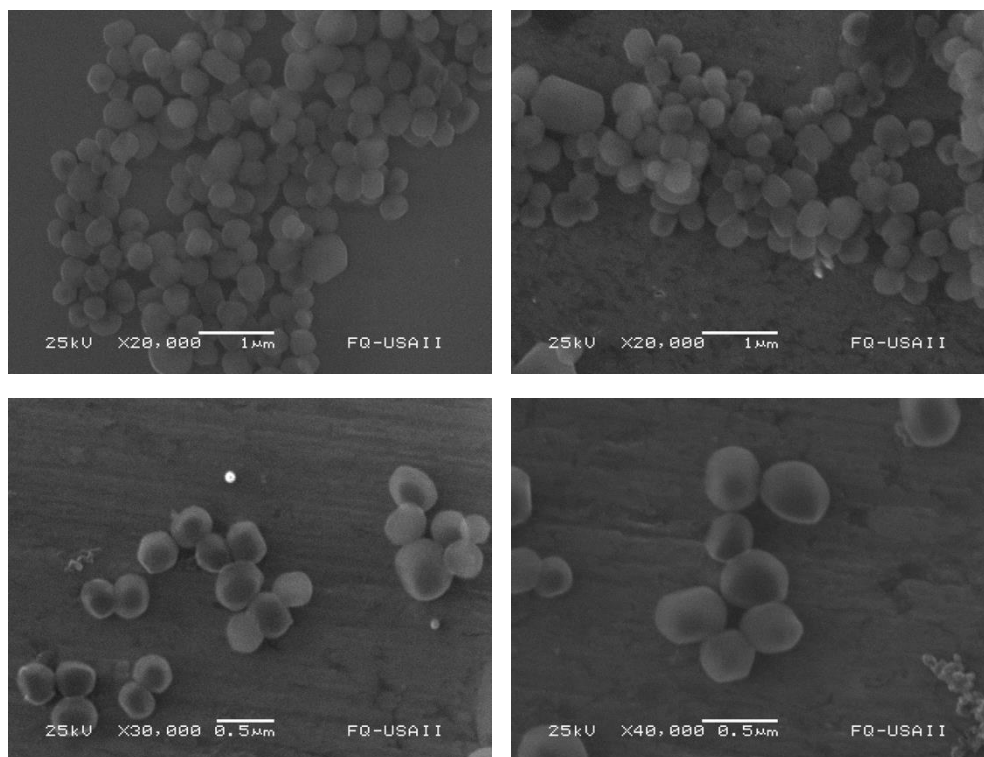
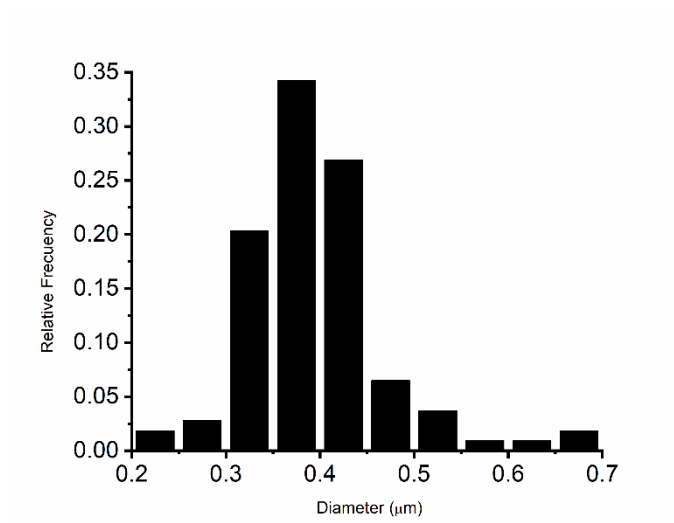**Figure S15** SEM images of functionalized silica **SiO$_2$-APTES.**

Figure S16 Histogram of the **SiO$_2$-APTES** particle size distribution. Mean diameter = 393±74 nm (for 108 particles)

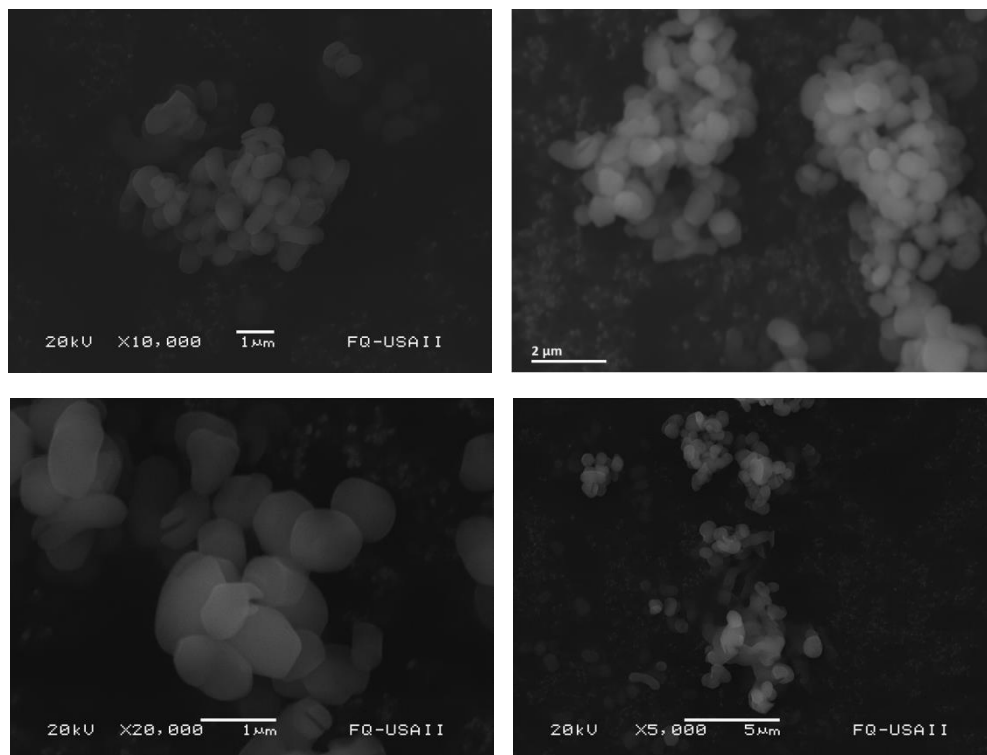**Figure S17** SEM images of functionalized silica **SiO$_2$-(CH$_2$)$_3$-NAM.**
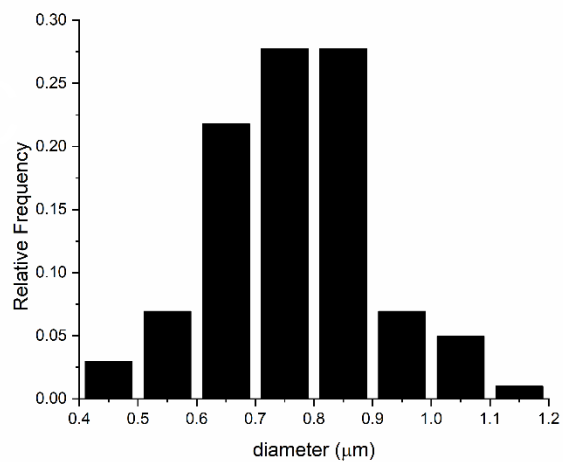
Figure S18 Histogram of the **SiO$_2$-(CH$_2$)$_3$-NAM** particle size distribution. Mean diameter = 767±137 nm (for 101 particles)

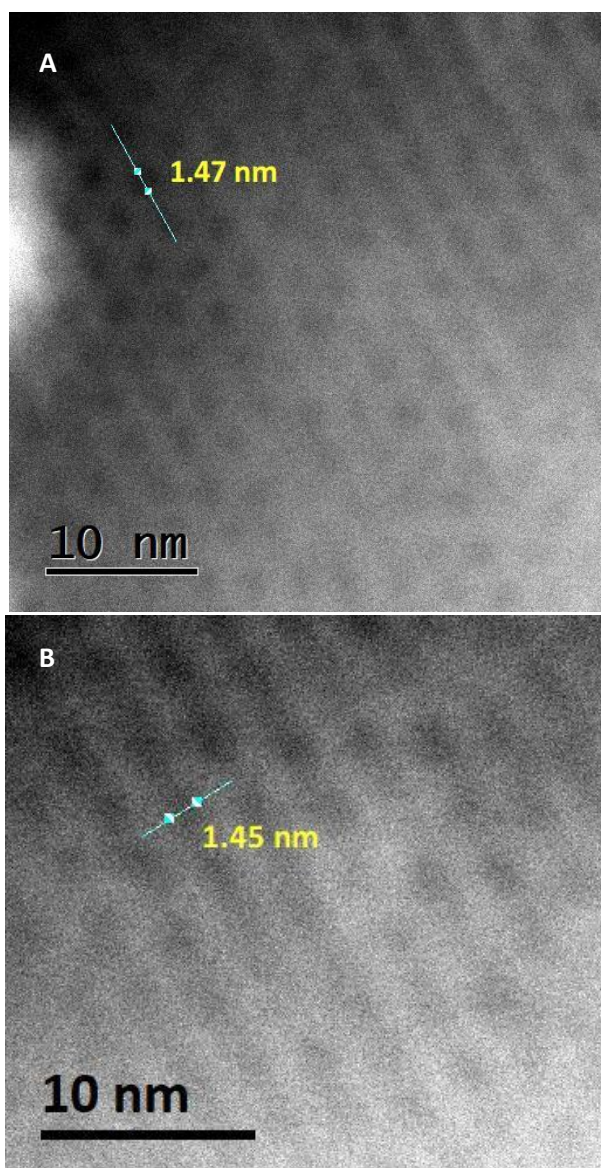# 6. TEM images and EDX analysis

Figure S19 HAADF-STEM images of pristine **SiO$_2$** and FFT of **A-B** (Pore size measured determined by FFT = 1.4 nm).
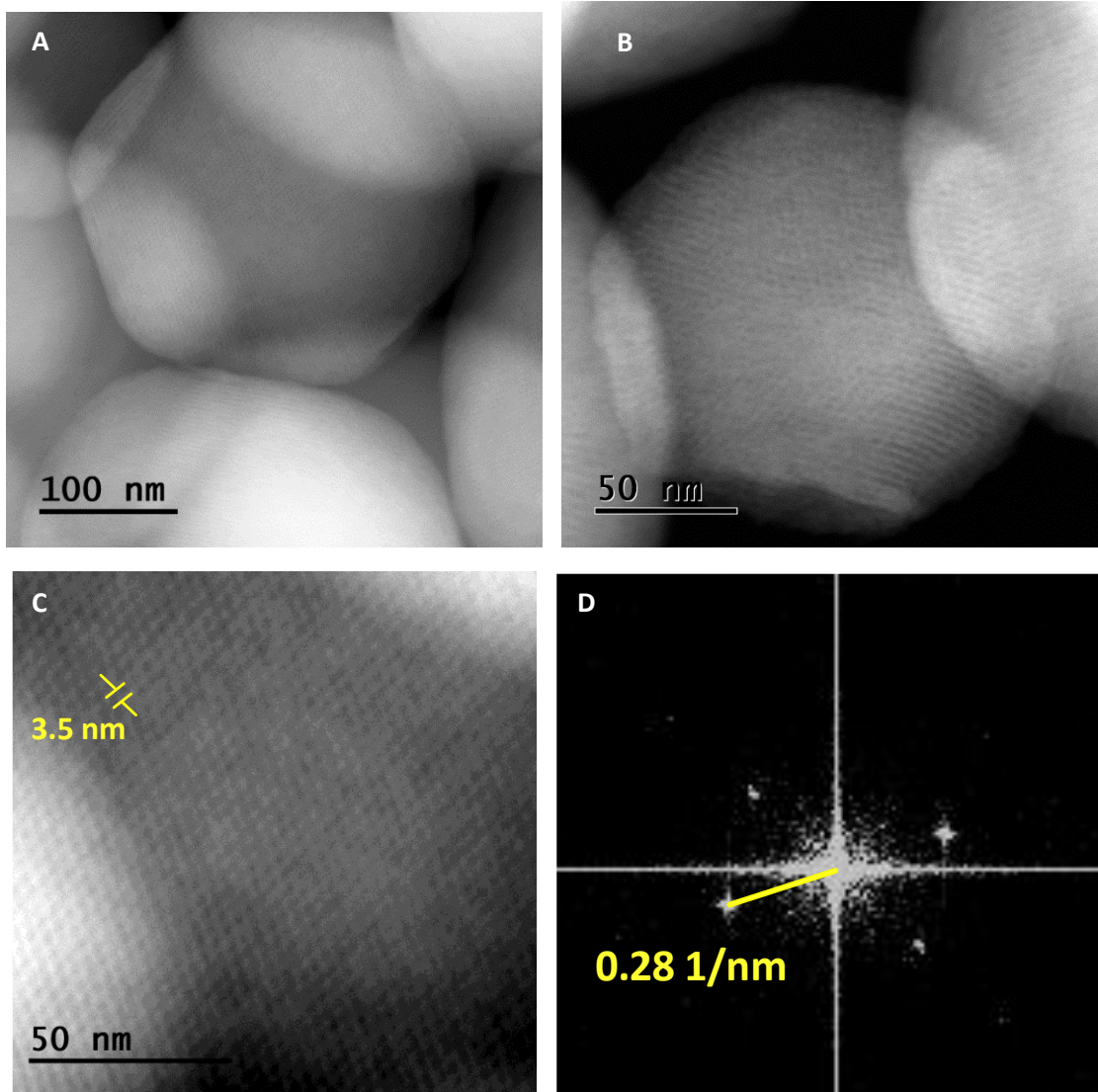
Figure S20 HAADF-STEM images of **SiO$_2$-APTES** (**A-C**) and FFT of **C.** (Pore size measured determined by FFT = 3.5 nm).
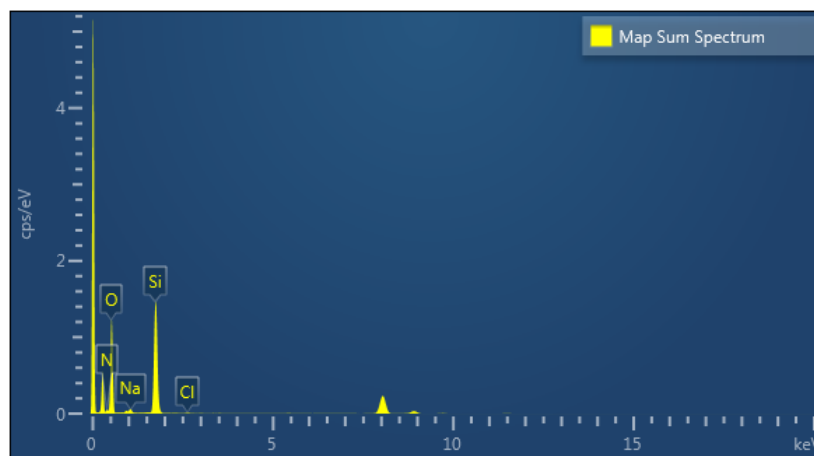

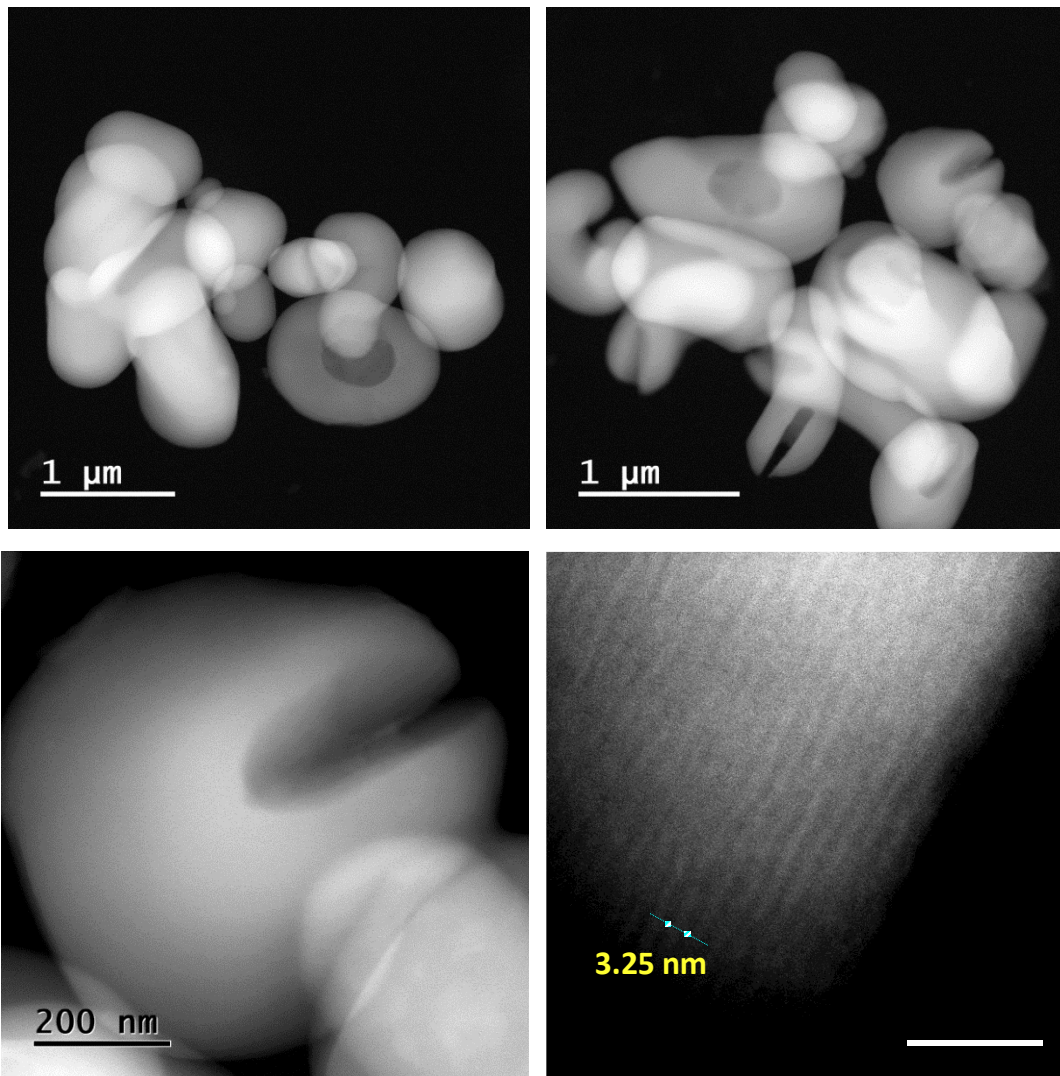**Figure S21** EDX element quantification of **SiO$_2$-APTES**.

Figure S22 HAADF-STEM images of **SiO$_2$-(CH$_2$)$_3$-NAM. (**Pore size determined by HAADF-STEM = 3.3 nm)
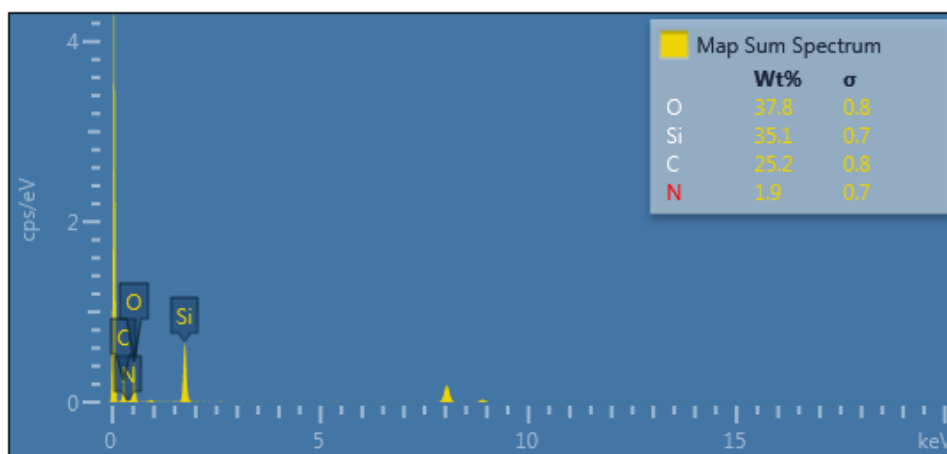
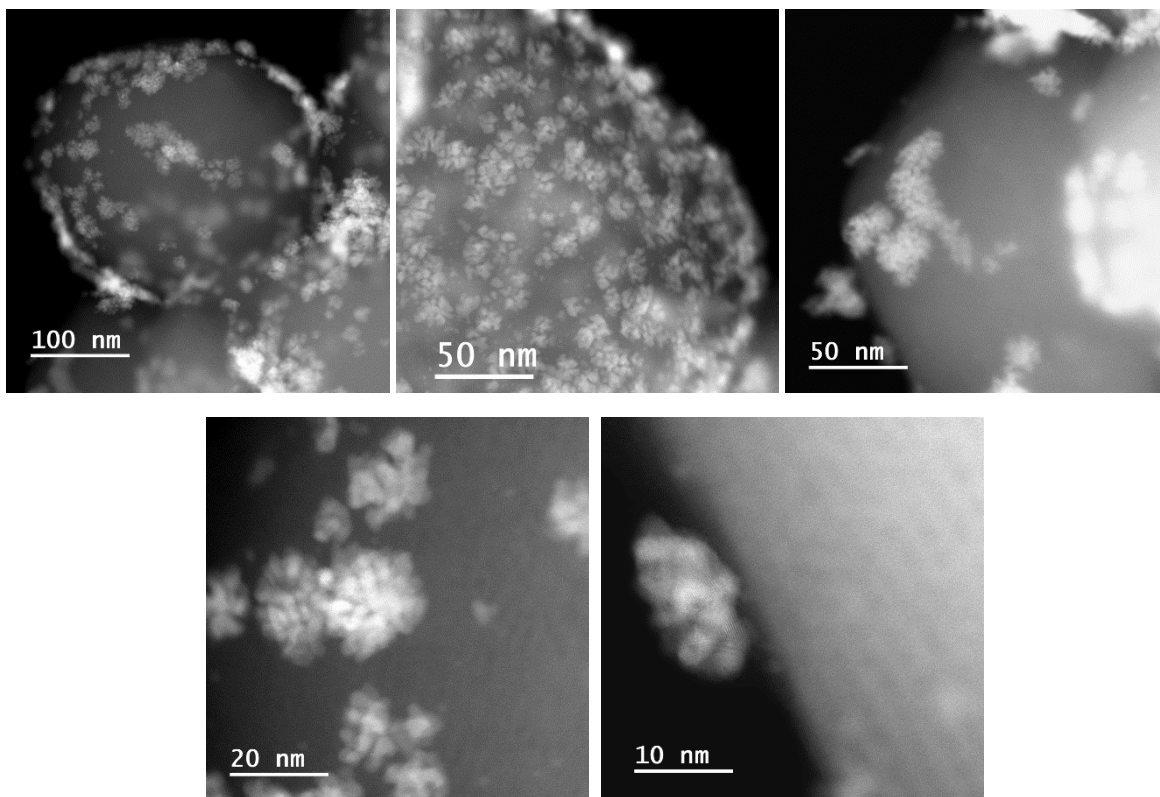**Figure S23** EDX element quantification of **SiO$_2$-(CH$_2$)$_3$-NAM**.

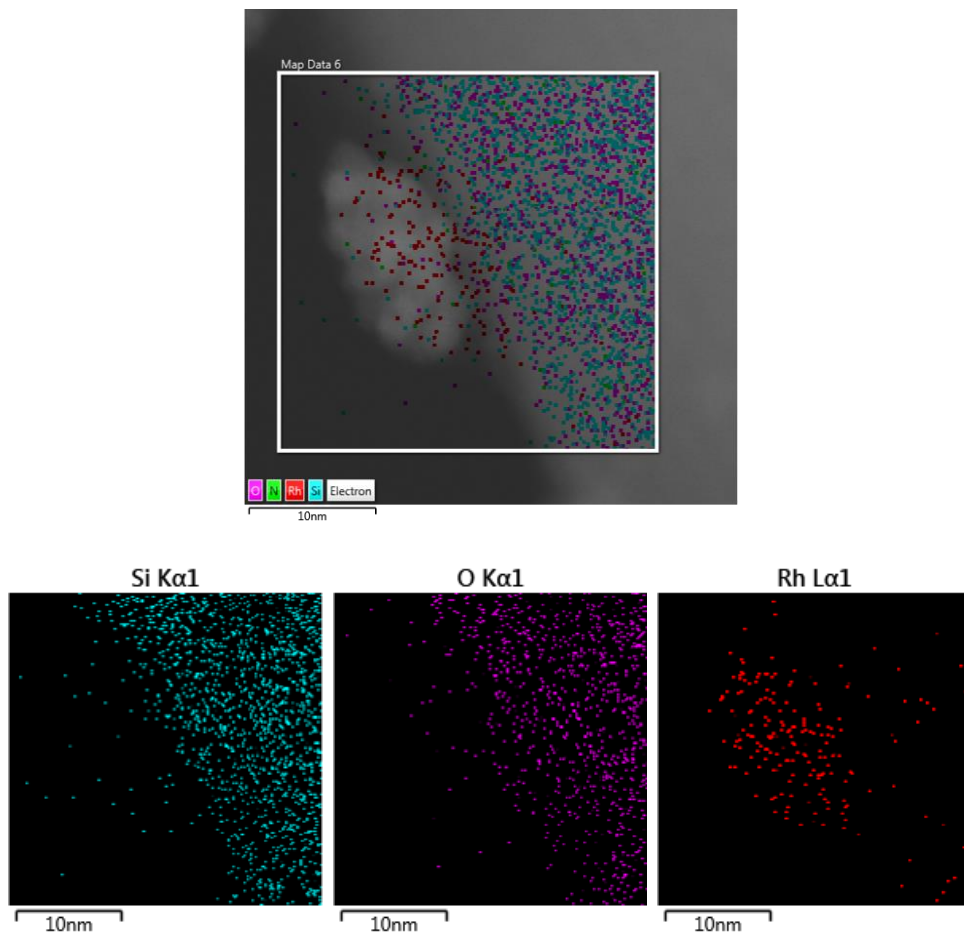**Figure S24** HAADF-STEM images of **RhNPs-A**. (no functionalization)

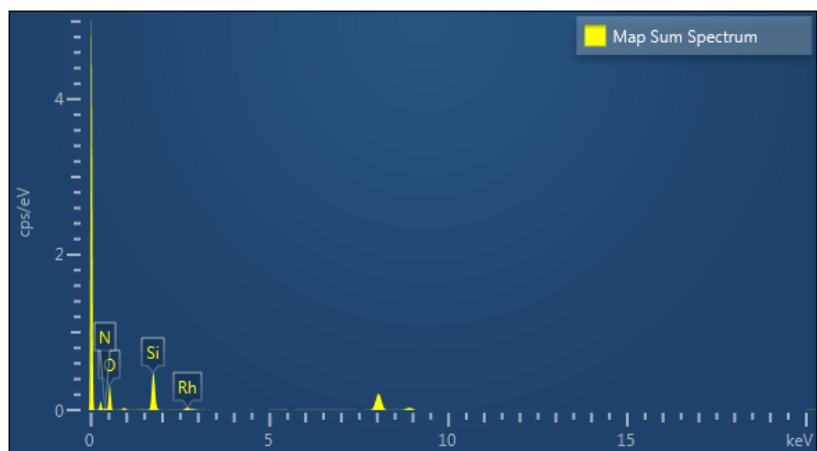**Figure S25** EDX element mapping images of **RhNPs-A**.(no functionalization)

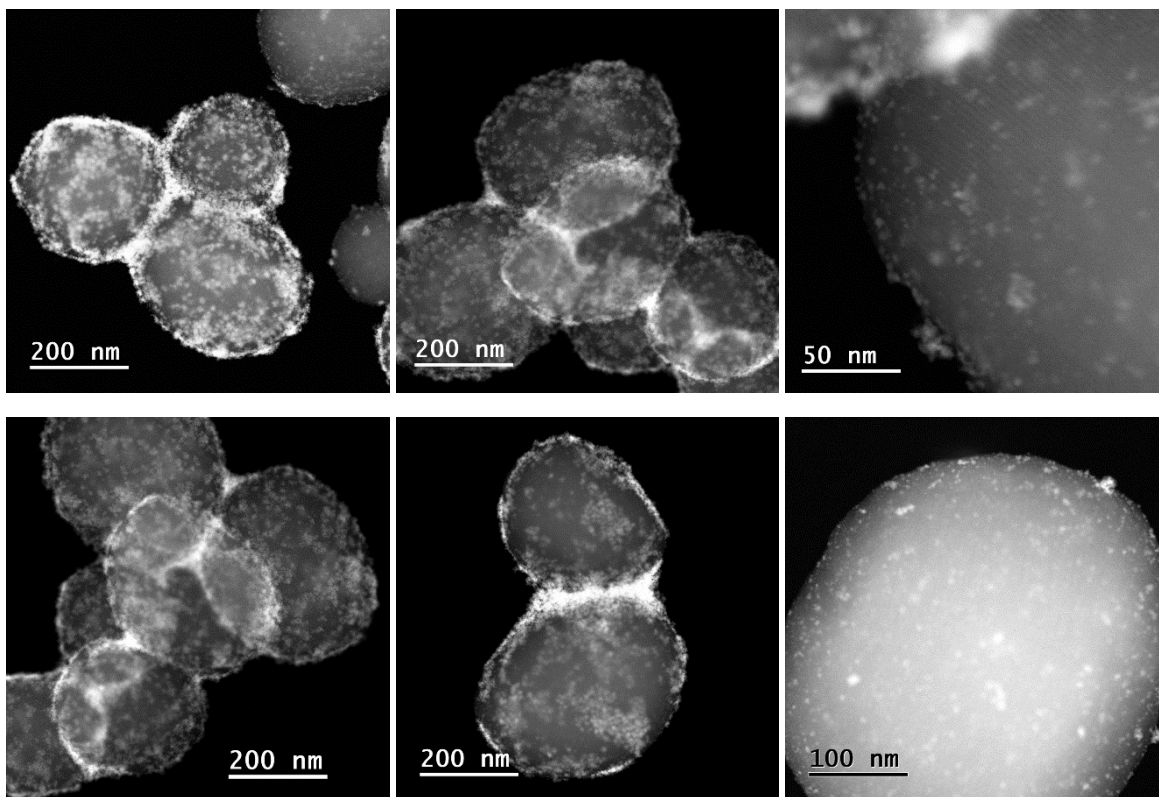**Figure S26** EDX element quantification of **RhNPs-A**. (no functionalization)

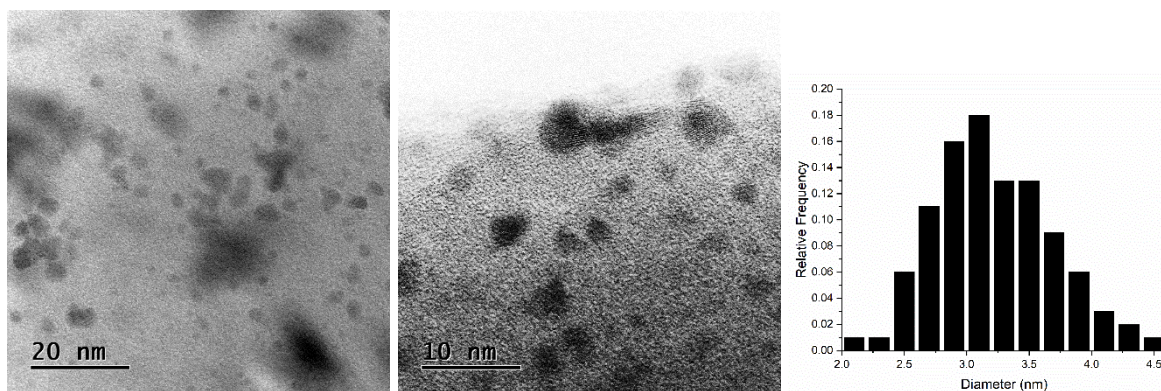**Figure S27** HAADF-STEM images of **RhNPs-B.**

Figure S28TEM images magnification and histogram of the **RhNPs-B** particle size distribution. Mean diameter = 3.2±0.5 nm (for 100 particles)
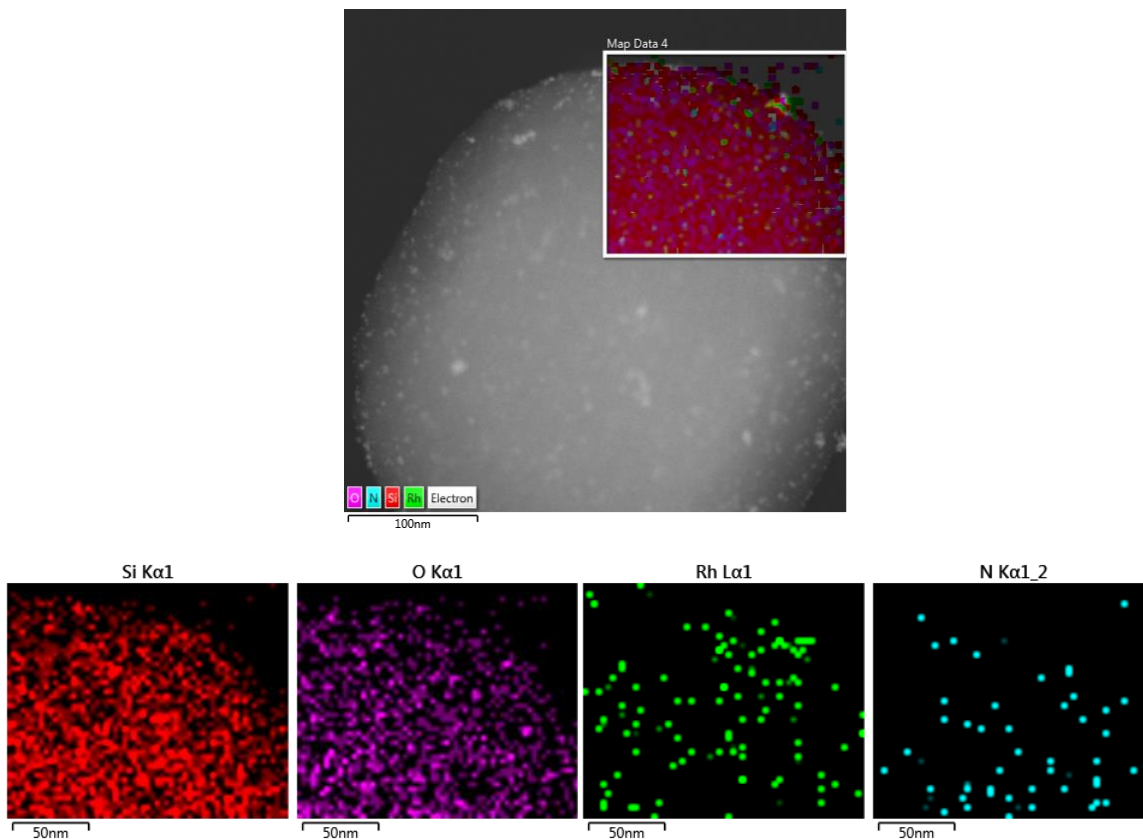
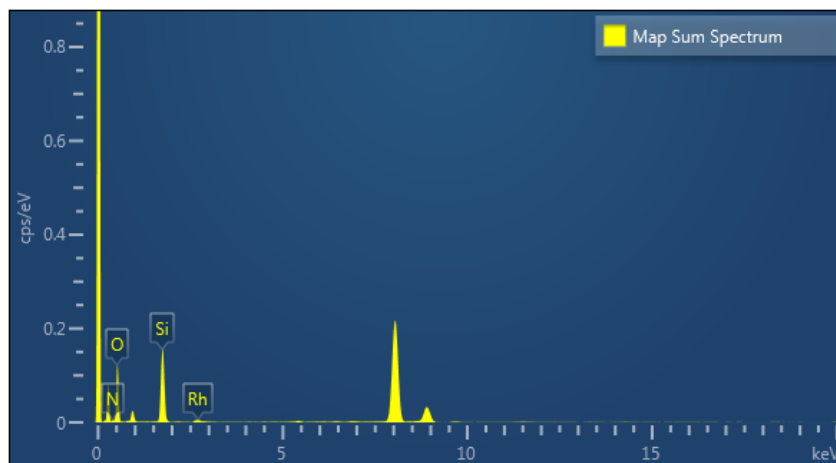Figure S29 EDX element mapping images of **RhNPs-B**.

Figure S30 EDX element quantification of **RhNPs-B**.

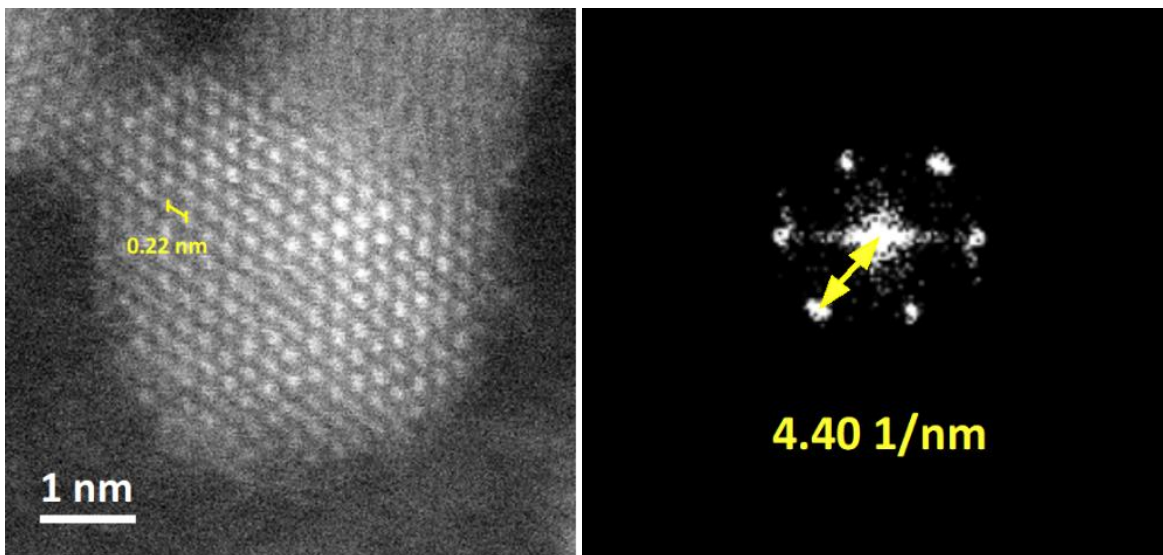**Figure S31** HR-HAADF-STEM of one Rh nanoparticle in **RhNPs-B.**

Figure S32 HAADF-STEM images of **RhNPs-C**
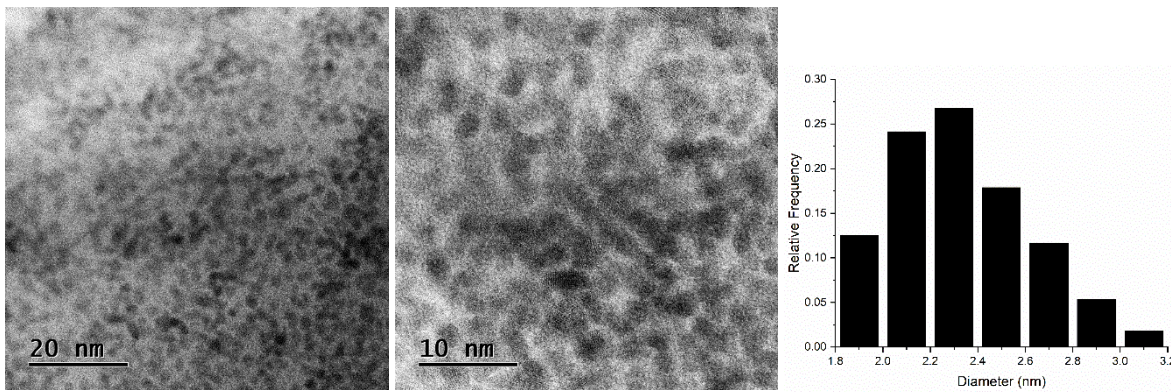
Figure S33 TEM images magnification and histogram of the **RhNPs-C** particle size distribution. Mean diameter = 2.3±0.3 nm (for 112 particles)

Si Kα1   O Kα1   Rh Lα1   N Kα1_2

Figure S34 EDX element mapping images of **RhNPs-C**.

Figure S35 EDX element quantification of **RhNPs-C**.
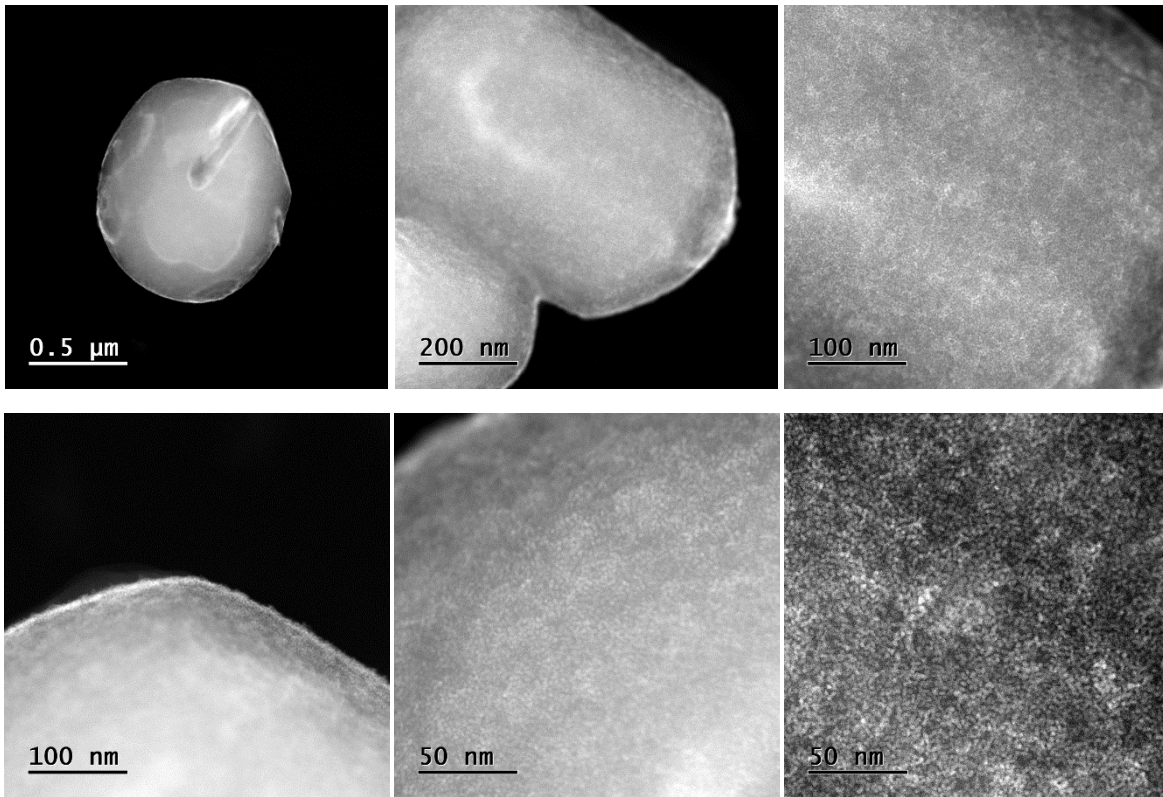
Figure S36 HR-HAADF-STEM of Rh nanoparticles in **RhNPs-C.**

7. BET isotherms of supported RhNPs.
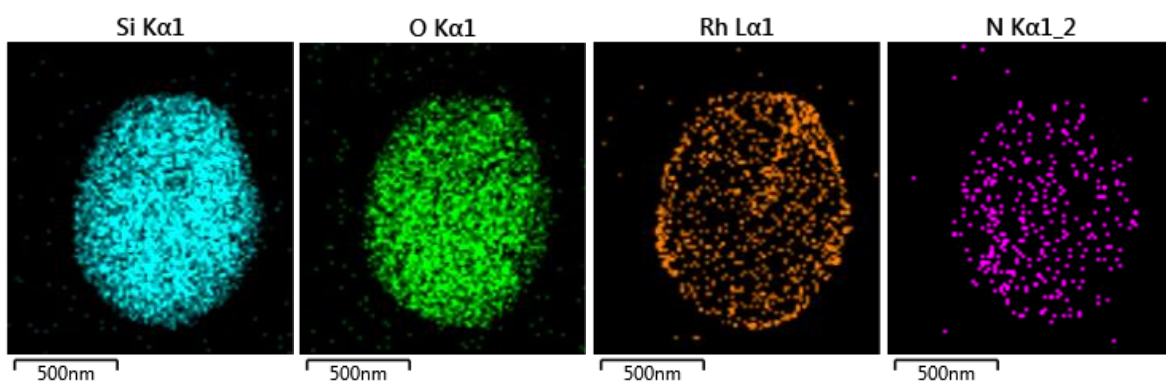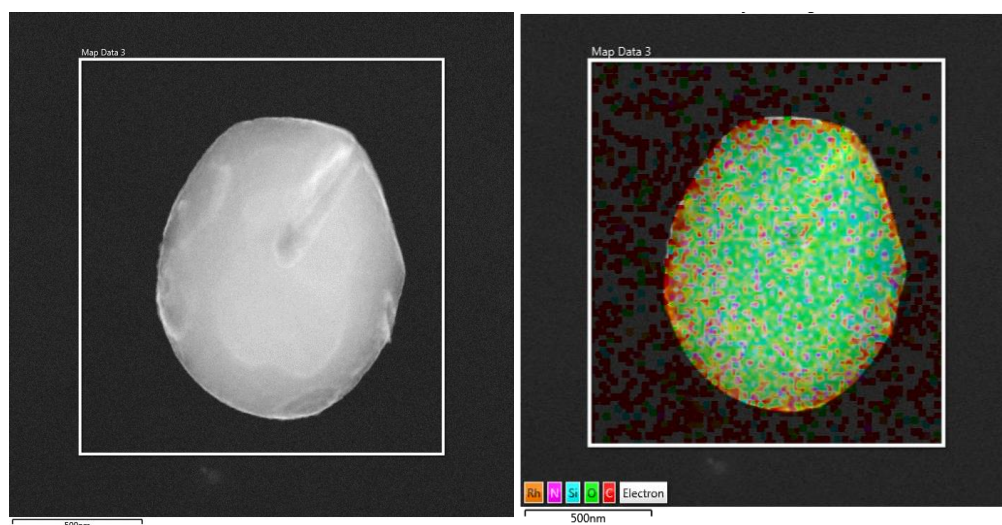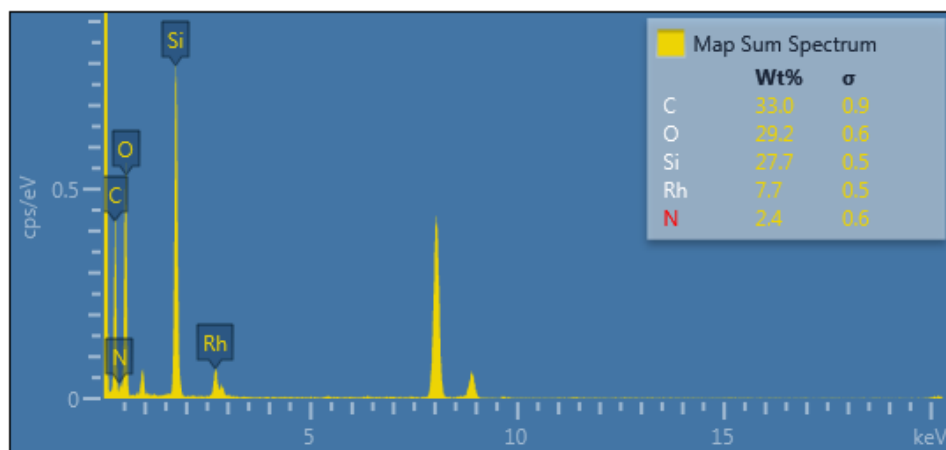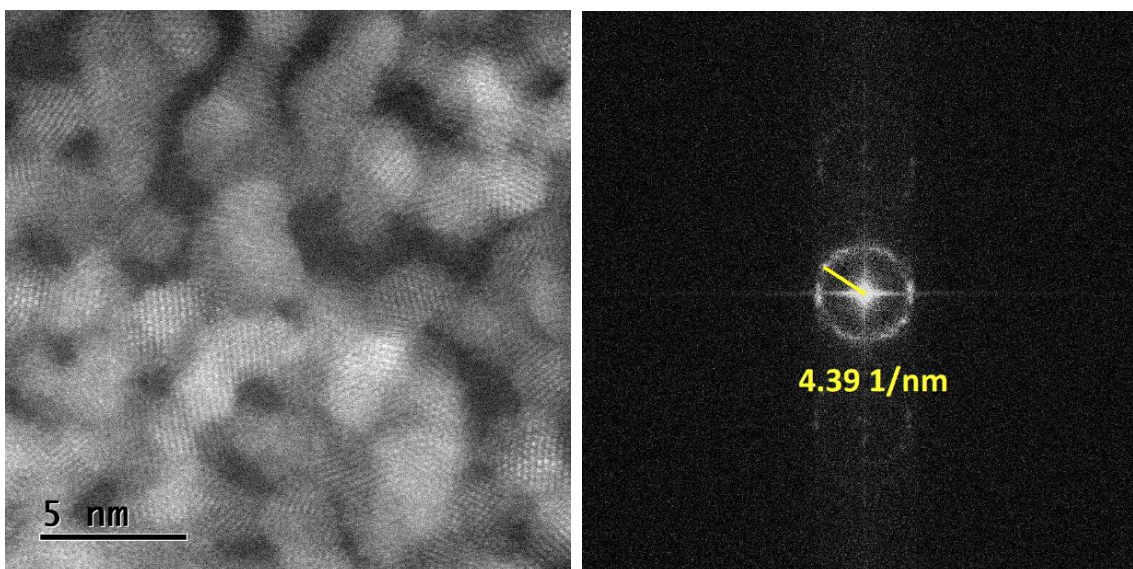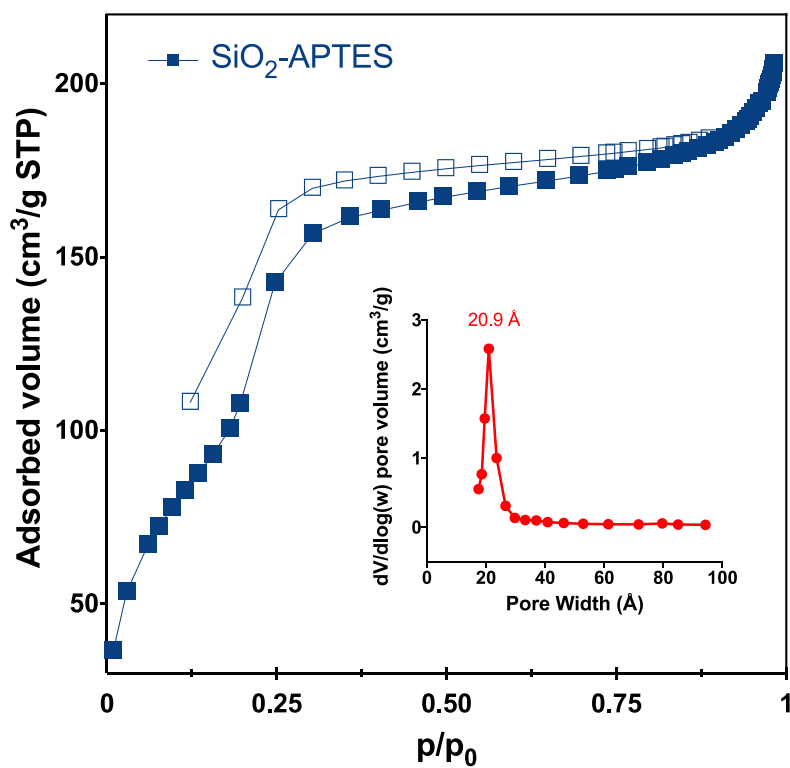

Figure S37 Adsorption-desorption isotherms of SiO₂-APTES with pore size.
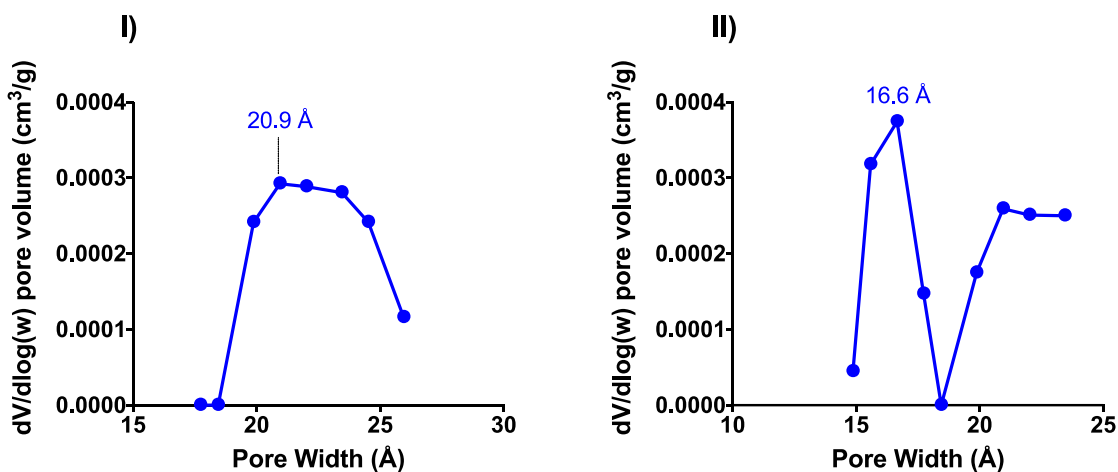
Figure S38 Pore size of I) RhNPs-B and II) RhNPs-C

**Table S5** BET isotherms analysis of supported RhNPs on functionalized silicas.
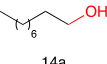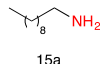
Entry	Material	S_{BET} (m^2 g^{-1})	Pore width (nm)
1	**SiO₂-APTES**	424	2.09 [a]
2	**RhNPs-A**	n.d.	n.d.
3	**RhNPs-B**	16	2.09 [b]
4	**RhNPs-C**	9	1.66 [b]

[a] Calculated using Brunauer–Emmett– Teller (BET) model on the adsorption branch in the range of relative pressure (P/Po) from 0.06 to 0.196..
[b] Calculated using the Non-Local Density Functional Theory model (Tarazona NLDFT, Cylindrical Pores, Esf = 30.0K).

8. Selected catalytic experiments

Table S6 Substrates that are not susceptible to hydrogenation by **RhNPs-B** at low pressure.

Entry	Substrate	Main Product	Conversion (%) [a]	Sel. to main product (%) [a]
1	12a	12b	1	N.D.
2	13	13a	0	N.D.
3	14	14a	0 (0[b])	N.D.
4	15	15a	0	N.D.

Reaction conditions: 2 mmol of substrate, 5 mg of **RhNPs-B** (0.07 mol%), H₂ (5 bar), 2 mL of **toluene**, 100 °C. [a] Determined by GC using FID detector. [b] Using **RhNPs-B** or **RhNPs-C** at 40 bar of H₂ no conversion are observed.

Table S7 Optimization of reaction conditions at low pressure of the catalyzed hydrogenation of acetophenone.
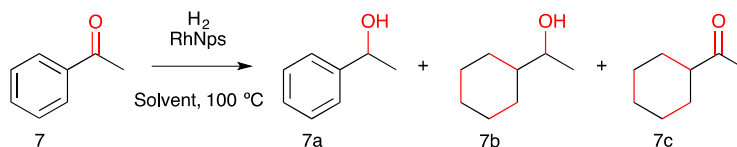
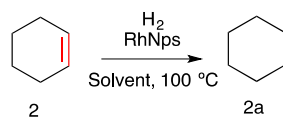| Entry	Catalyst	Substrate 7 (mmol)	Time(h)	Solvent	%Conv. [a]	%Selectivity [a]			TOF (h^{-1})[b]
						7a	7b	7c	
1	**Pristine SiO$_2$**	2	2	toluene	0	-	-	-	0
2	**SiO$_2$-APTES**	2	2	toluene	0	-	-	-	0
3	**RhNPs-A**	2	2	toluene	10	80	0	20	48
4	**RhNPs-B**	2	2	toluene	98	81	8	11	560
5	**RhNPs-C**	2	2	toluene	81	93	5	2	219
6	**RhNPs-B**	1	1	toluene	62	89	1	10	389
7	**RhNPs-B**	2	1	toluene	64	91	1	2	822
8	**RhNPs-B**	5	1	toluene	42	95	0	5	1408
9	**RhNPs-B**	10	1	toluene	17	94	0	6	1128
10	**RhNPs-B**	1	2	toluene	99	64	21	15	223
11	**RhNPs-B**	2	2	DMC	48	85	0	15	288
12	**RhNPs-B**	2	2	H$_2$O	88	94	1	5	584
13	**RhNPs-B**	2	2	glycerol	38	97	0	3	260
14	**RhNPs-B**	2	2	EtOH	84	88	7	5	521
15	**RhNPs-B**	2	2	heptane	64	97	2	1	438
16	**RhNPs-C**	2	2	heptane	>99	70	23	5	493

Reaction conditions: 2 mmol of acetophenone (**7**), 5 mg of catalyst [**RhNPs-A** (0.10 mol%); **RhNPs-B** (0.07 mol%); **RhNPs- C** (0.18 mol%)], **H$_2$ (5 bar)**, 100 °C. [a] Determined by GC using FID detector. [b] TOF= mmol of principal product x (mmol of Rh x h)$^{-1}$

Table S8 RhNPs-B catalyst reuse in the hydrogenation of cyclohexene in toluene.
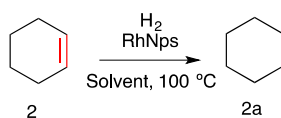
Run	Conversion (%)[a]	TOF (h^{-1}) [c]
1	99	705
2	99	705
3	99	705
4	99	705
5	99	705

Reaction conditions: 2 mmol of cyclohexene (2), 5 mg of **RhNPs-B** (0.07 mol%), 2 mL of **toluene**, H$_2$ (5 bar), 100 °C, 2h. [a] Determined by GC using FID detector. [b] At the end of each reaction all volatiles are evaporated and collected for GC analysis then new acetophenone and toluene are added. [c] TOF= mmol of principal product x (mmol of Rh x h)$^{-1}$

Table S9 RhNPs-C catalyst reuse in the hydrogenation of cyclohexene in heptane.

$$\underset{\textbf{2}}{\text{cyclohexene}} \xrightarrow[\text{Solvent, 100 °C}]{\underset{\text{RhNps}}{H_2}} \underset{\textbf{2a}}{\text{cyclohexane}}$$

Run[b]	Conversion (%)[a]	TOF (h^{-1}) [c]
1	99	270
2	99	270
3	99	270
4	99	270
5	99	270

Reaction conditions: 2 mmol of cyclohexene (2), 5 mg of **RhNPs-C** (0.07 mol%), 2 mL of **heptane**, H$_2$ (5 bar), 100 °C, 2h. [a] Determined by GC using FID detector. [b] At the end of each reaction all volatiles are evaporated and collected for GC analysis then new acetophenone and heptane are added. . [c] TOF= mmol of principal product x (mmol of Rh x h)$^{-1}$

9. TEM images and EDX analysis after use in the catalyzed acetophenone hydrogenation
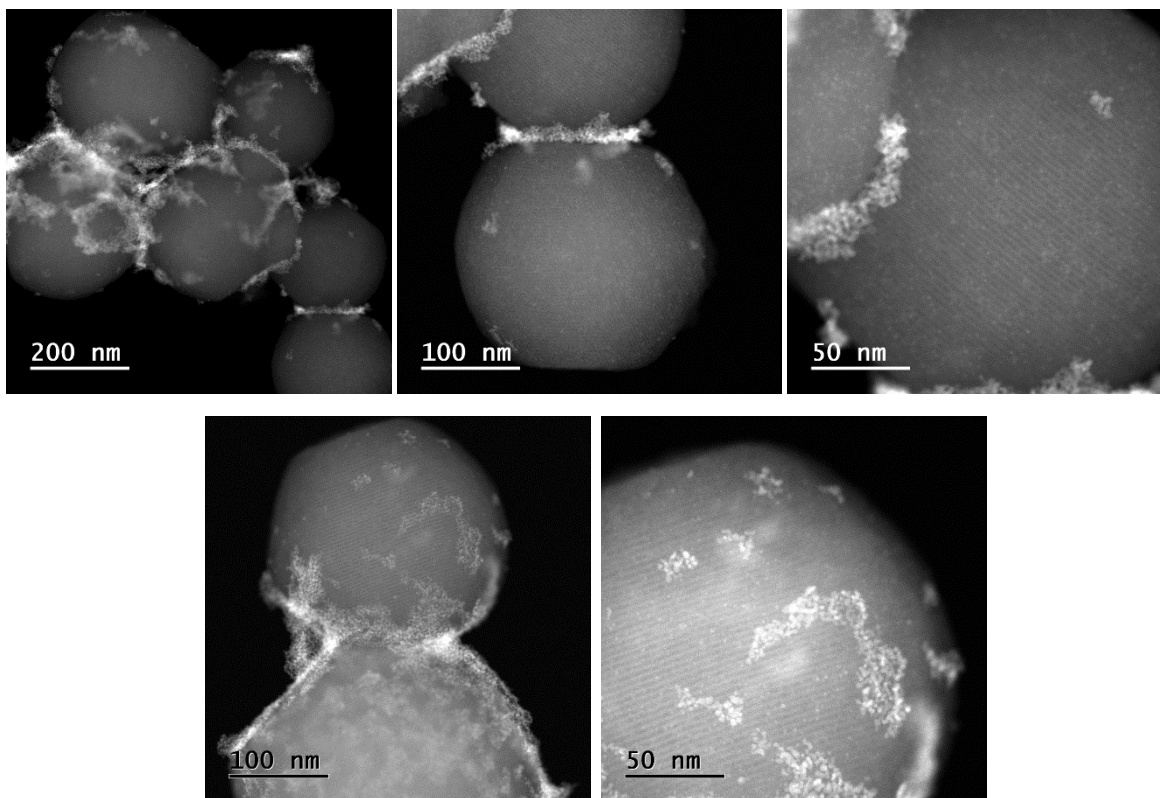

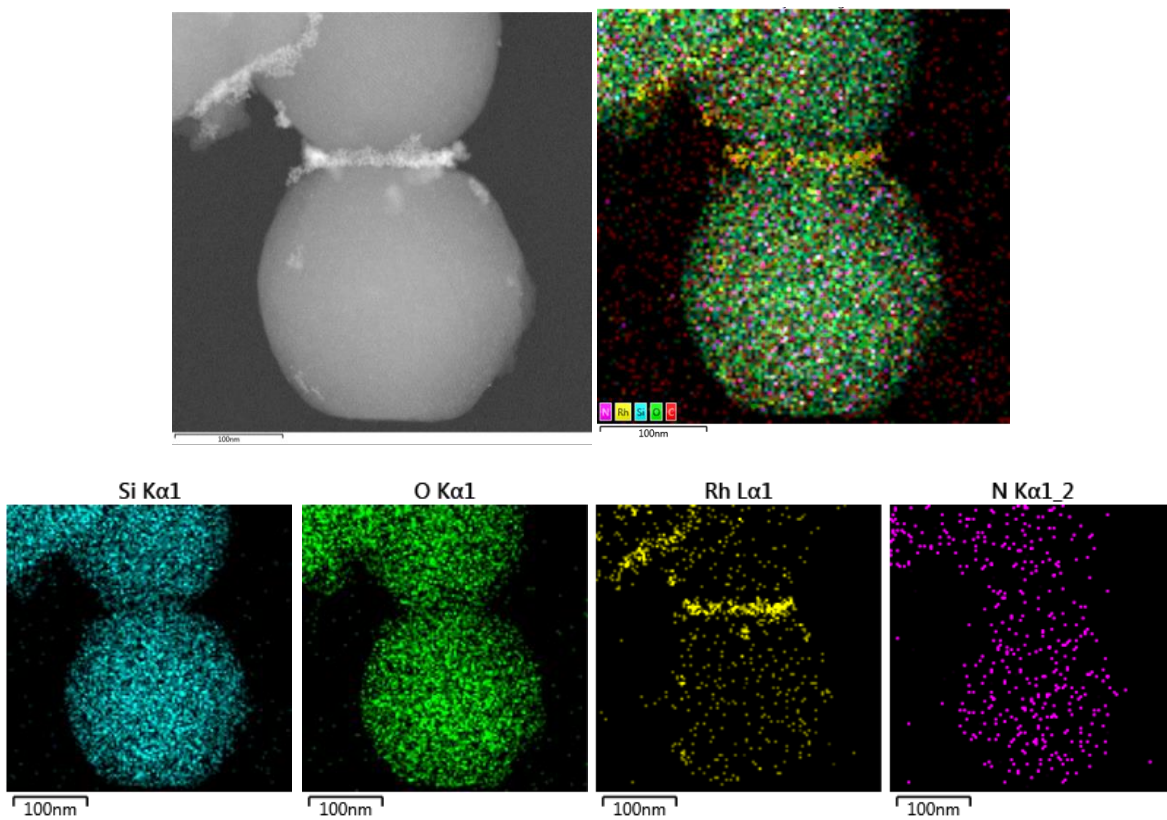**Figure S39** HAADF-STEM images of **RhNPs-B** after acetophenone hydrogenation (40 bar).

Si Kα1   **O Kα1**   **Rh Lα1**   **N Kα1_2**

Figure S40 EDX element mapping images of **RhNPs-B** after acetophenone hydrogenation (40 bar).

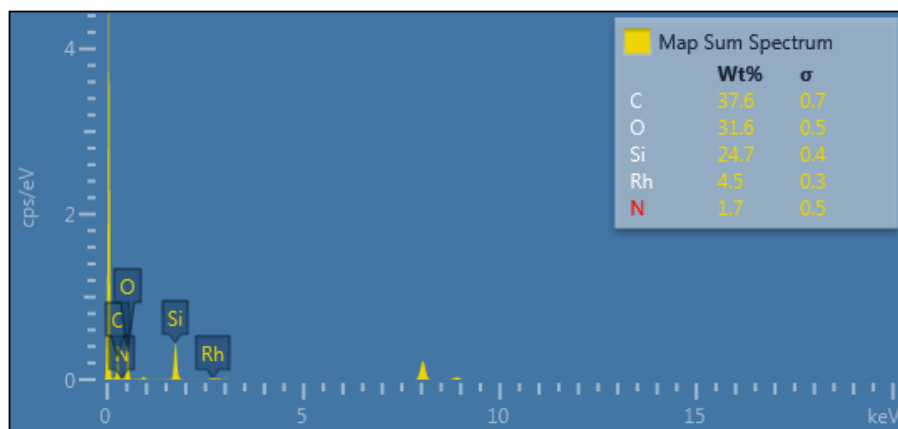| Map Sum Spectrum		
	Wt%	**σ**
C	37.6	0.7
O	31.6	0.5
Si	24.7	0.4
Rh	4.5	0.3
N	1.7	0.5

Figure S41 EDX element quantification of **RhNPs-B** after acetophenone hydrogenation (40 bar).
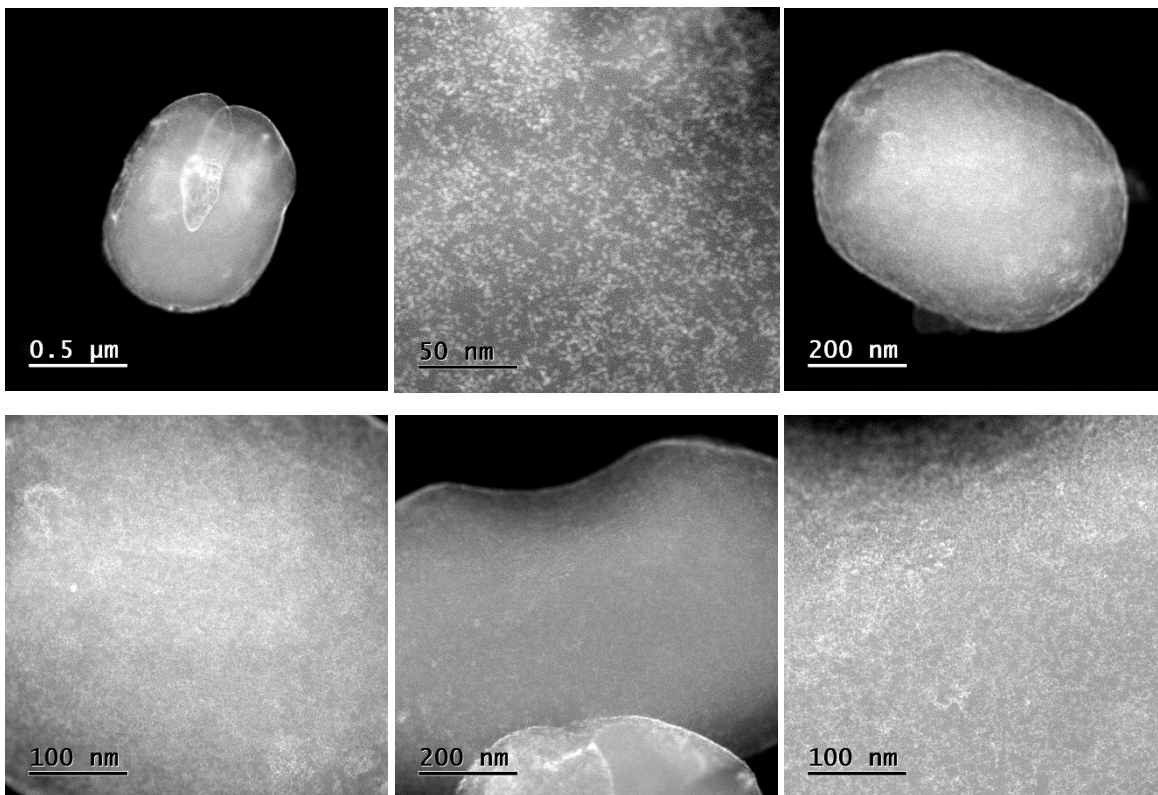
Figure S42 HAADF-STEM images of **RhNPs-C** after acetophenone hydrogenation (40 bar).
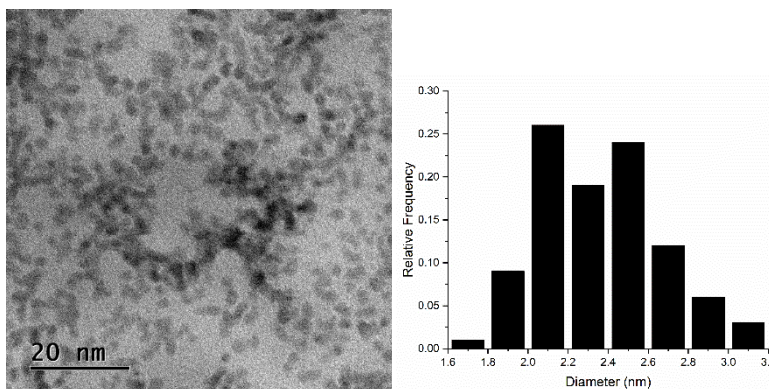

Figure S43 TEM image magnification and histogram of the **RhNPs-C** particle size distribution after acetophenone hydrogenation (40 bar). Mean diameter = 2.3±0.3 nm (for 100 particles)
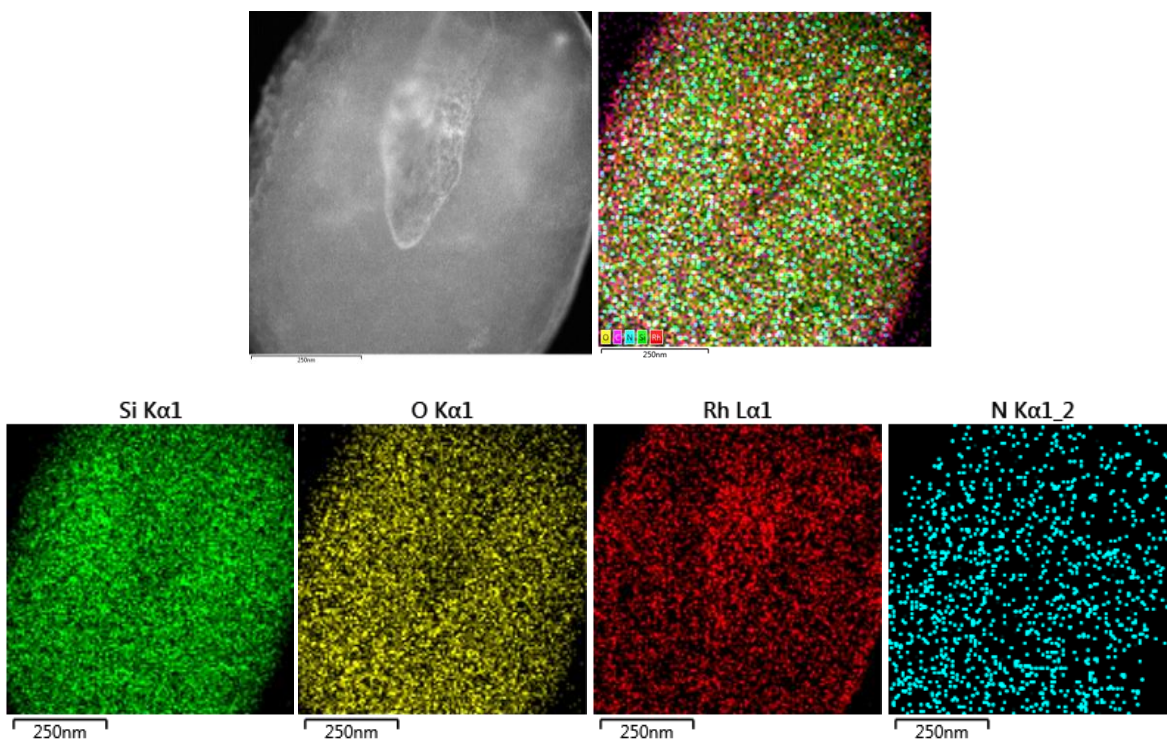
Si Kα1 O Kα1 Rh Lα1 N Kα1_2

Figure S44 EDX element mapping images of **RhNPs-C** after acetophenone hydrogenation (40 bar).

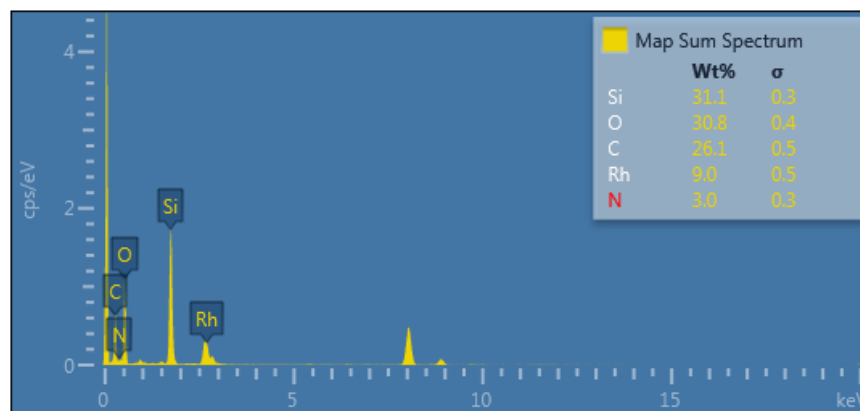| Map Sum Spectrum		
	Wt%	σ
Si	31.1	0.3
O	30.8	0.4
C	26.1	0.5
Rh	9.0	0.5
N	3.0	0.3

Figure S45 EDX element quantification of **RhNPs-C** after acetophenone hydrogenation (40 bar).