Electronic Supplementary Information

Etching Suppression as a Means to Pt Dendritic Ultrathin Nanosheets by Seeded Growth

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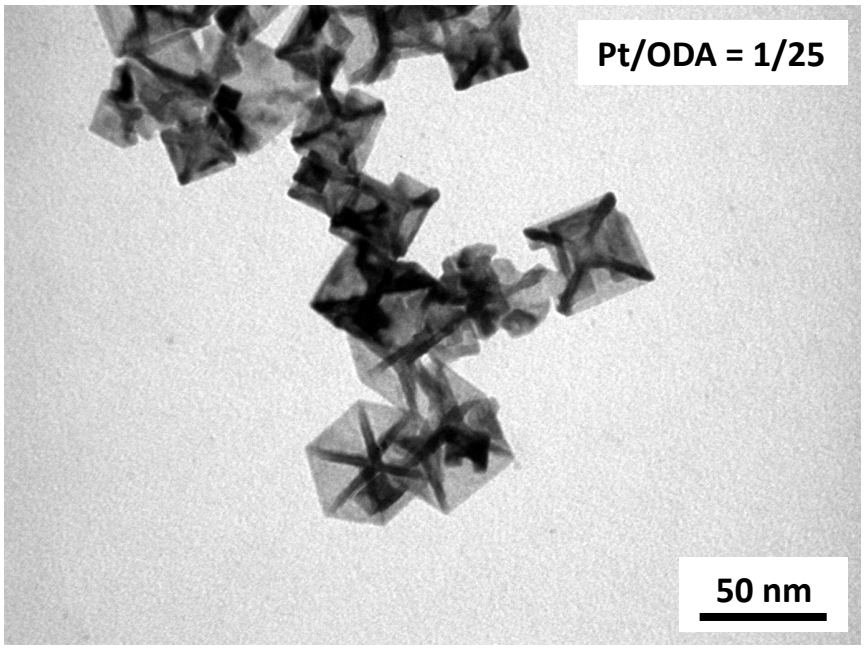


Figure S1. Concave nanocubes obtained by reduction of $PtCl_2$ in the presence of ODA at 20 °C under 3 bar H_2 (7 days reaction).

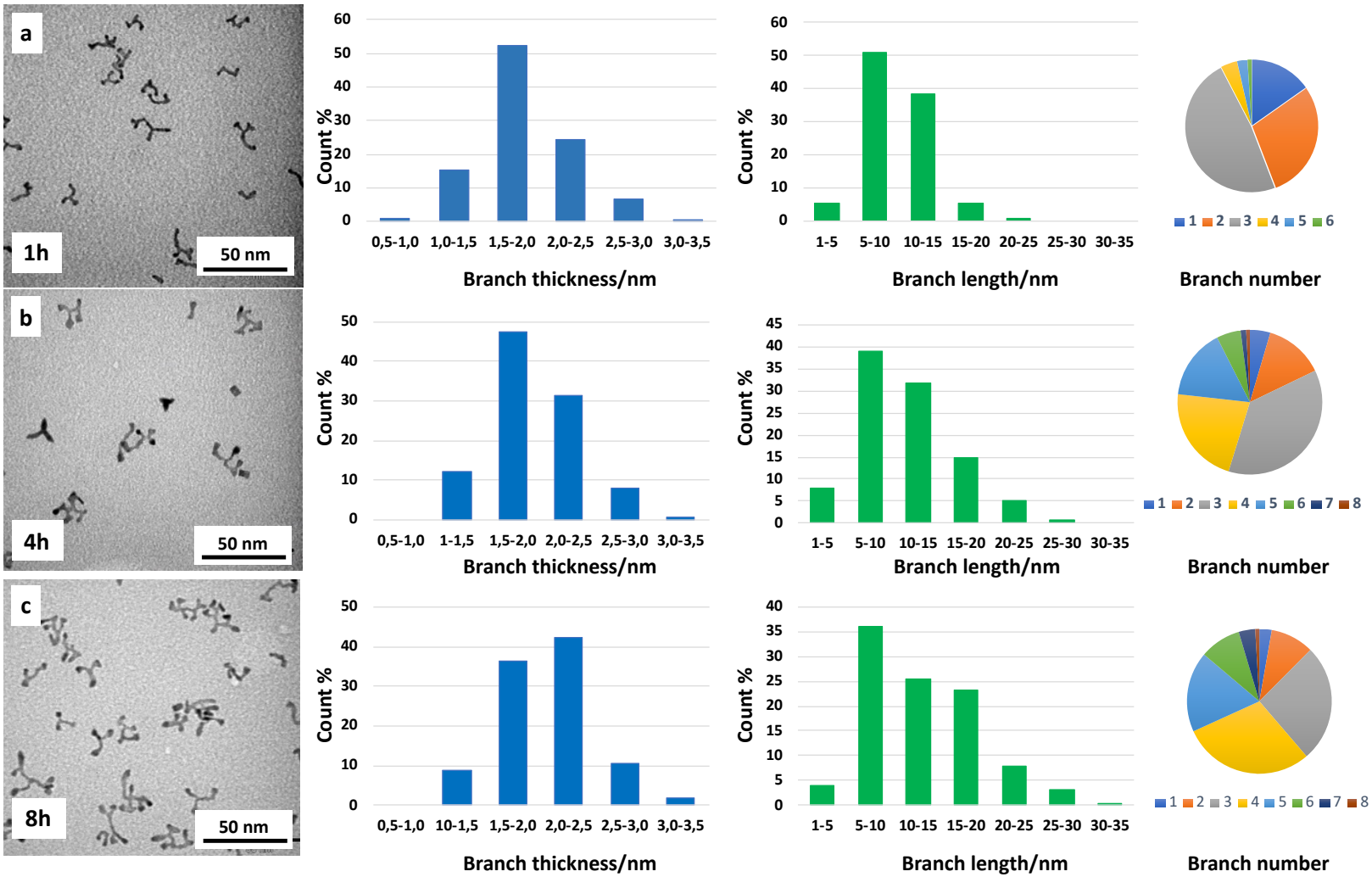


Figure S2. Time dependent evolution of the Pt multipods. (a) 1 h reaction. (b) 4 h reaction. (c) 8 h reaction.

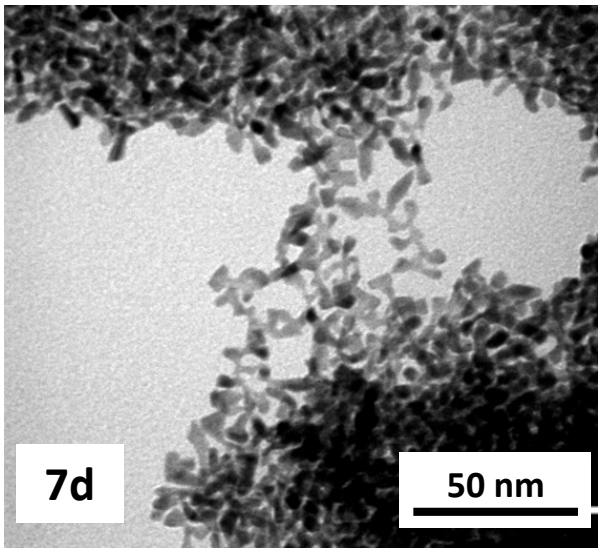


Figure S3. Agglomerated seeds after 7 days reaction.

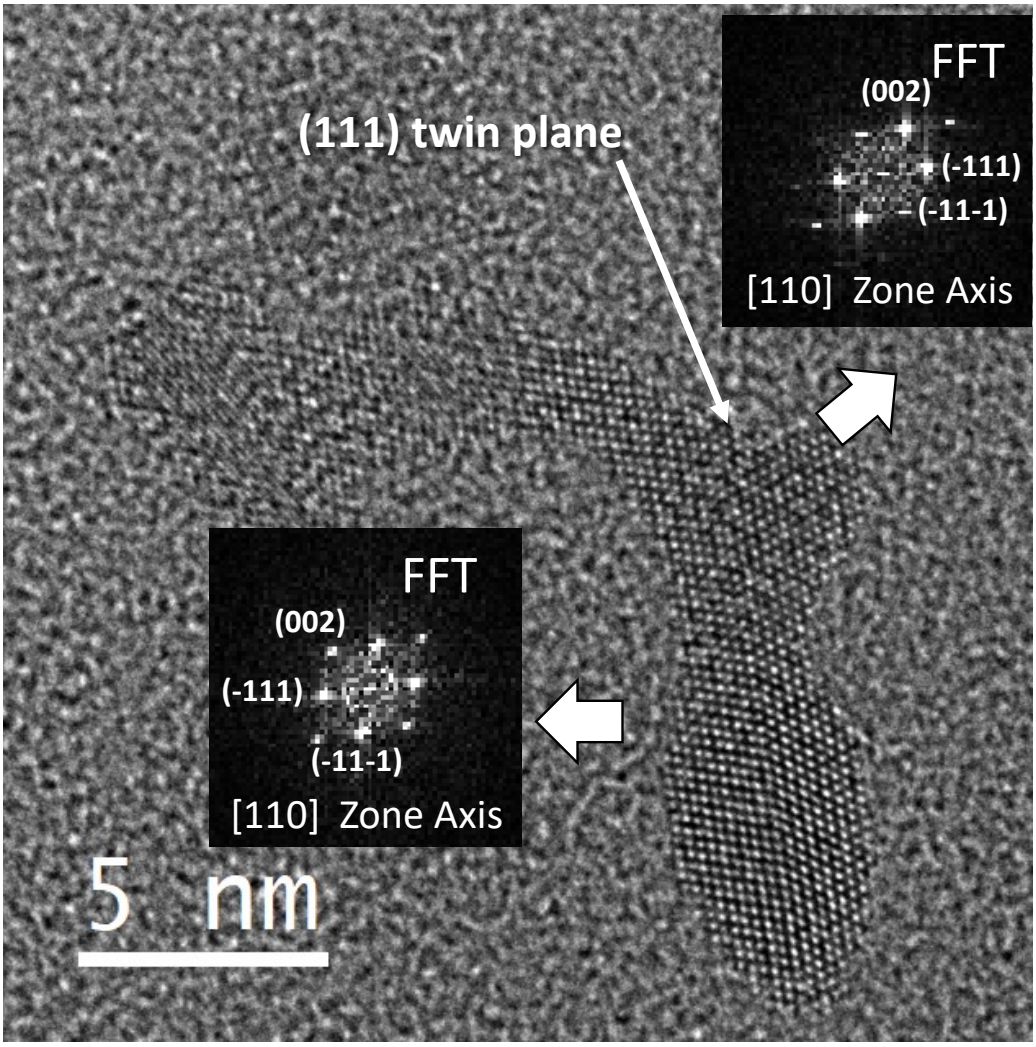


Figure S4. HRTEM image showing the presence of a $\{111\}$ twin plane on a nano-object obtained after 8 h of reaction.

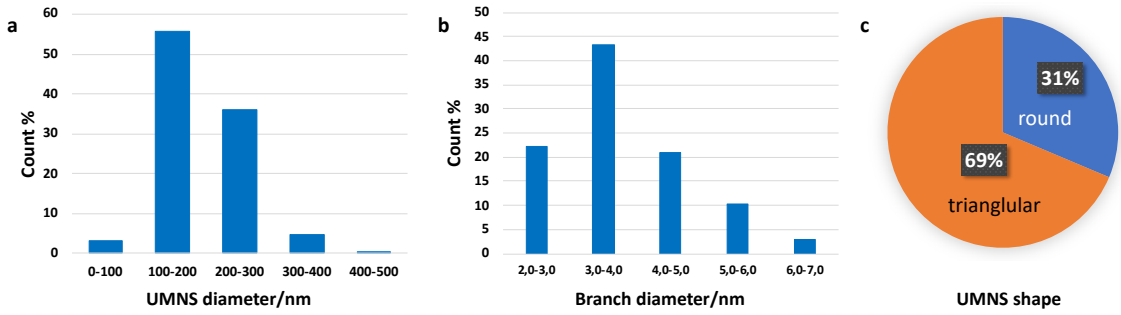


Figure S5. UMNS morphological characteristics. (a) diameter. (b) shape. (c) branch diameter.

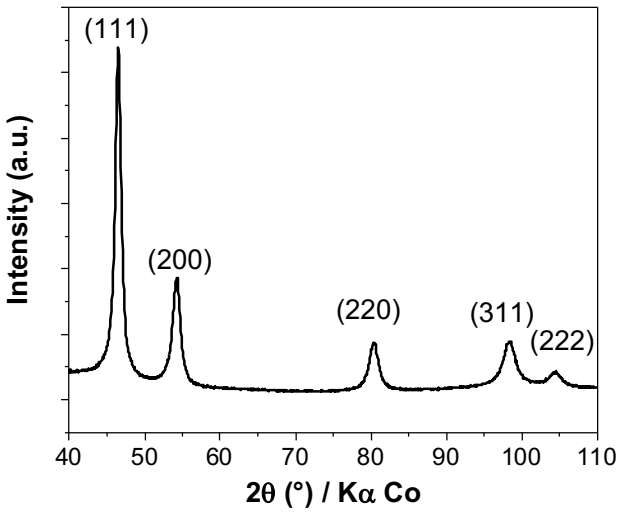


Figure S6. XRD of the Pt UMNS.

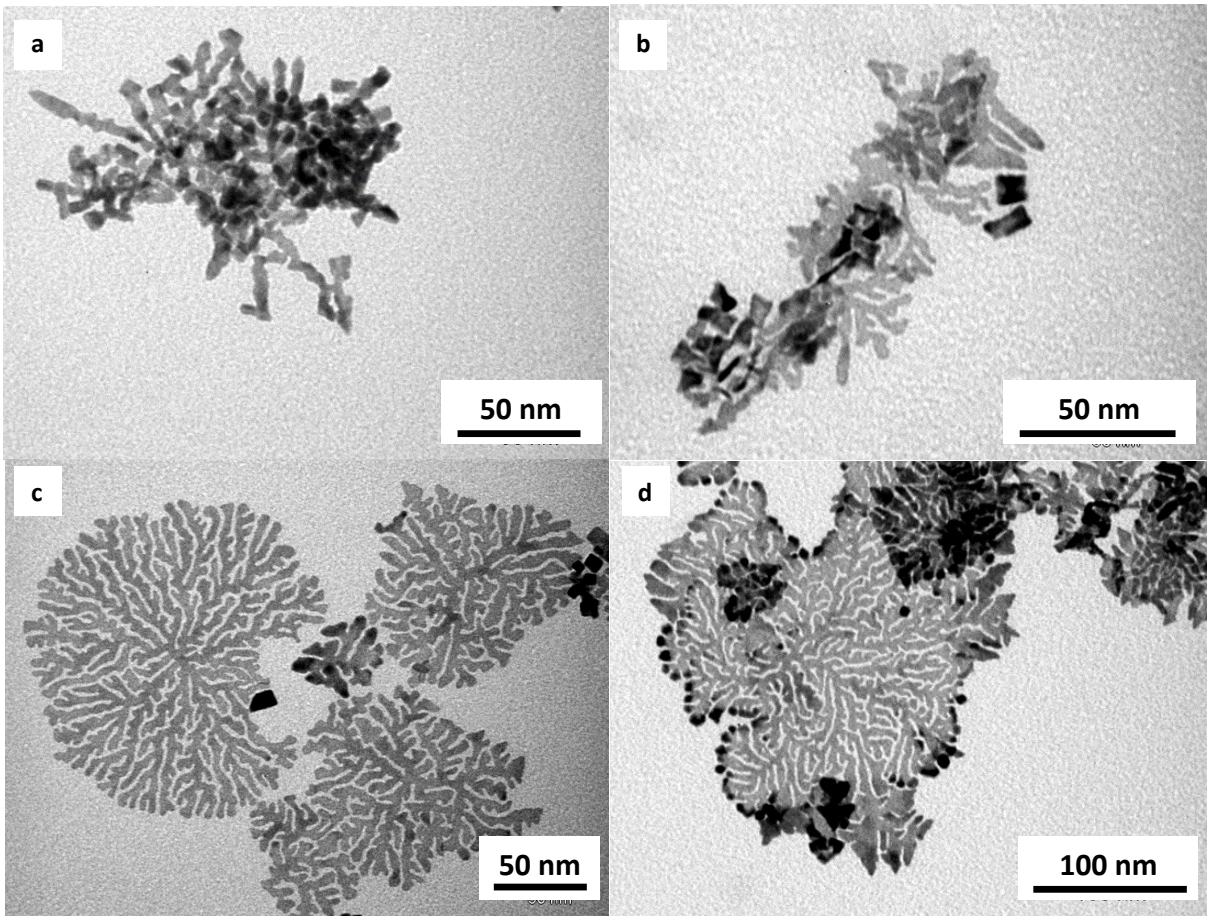


Figure S7. Time dependent evolution of the Pt UMNS. (a) 24 h reaction. (b) 48 h reaction; (c) 4 days reaction. (c) 7 days reaction.

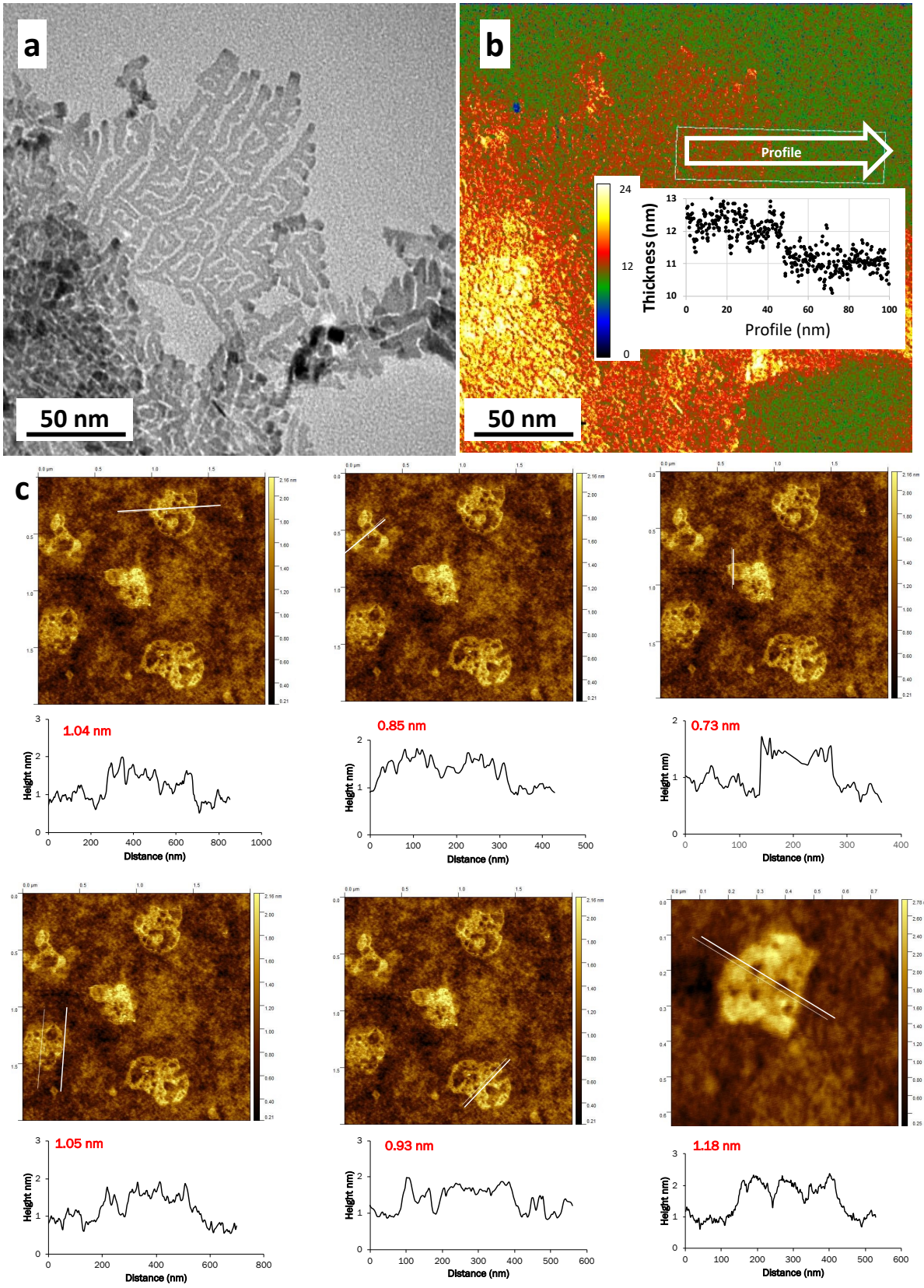


Figure S8. UMNS thickness. (a) TEM image of a Pt UMNS. (b) the corresponding thickness profile along line designated by the white arrow obtained through EFTEM. Point scattering is due to an average measurement of the thickness over all the pixels of the width of the

arrow. The UMNS thickness is obtained by subtracting the carbon membrane thickness (about 11 nm) from the total thickness (about 12 nm). (c) AFM of 6 UMNS and their corresponding mean thickness, as obtained by the profile measurement through the AFM Gwyddion program.

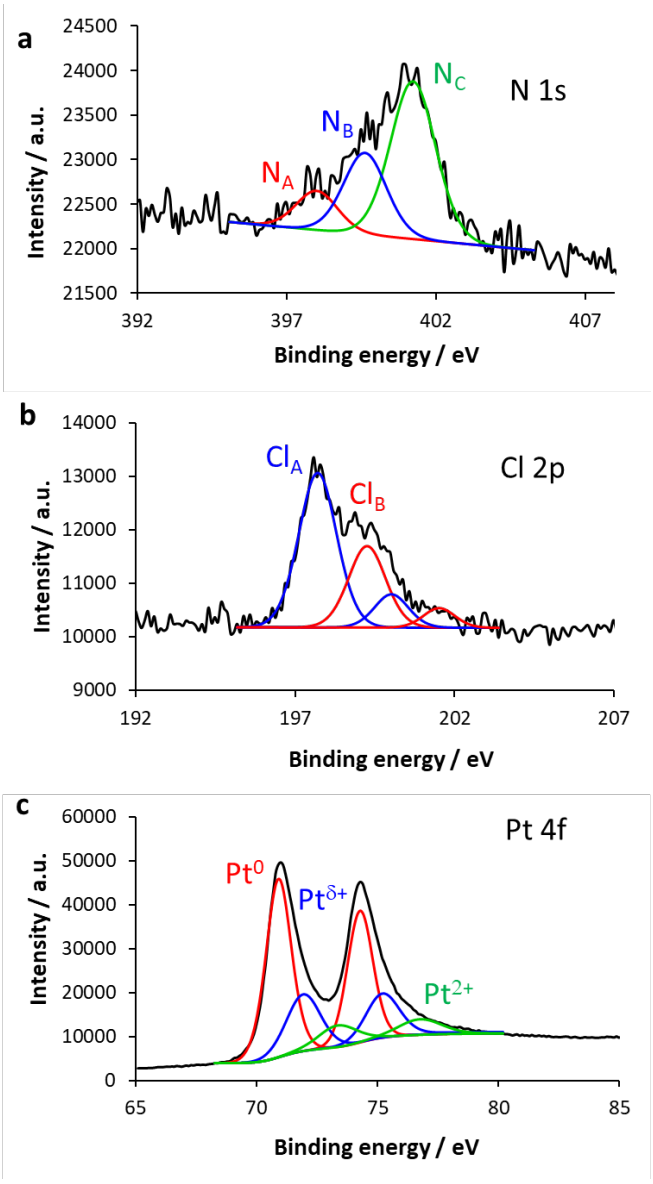


Figure S9. Pt UMNS XPS spectra. (a) N 1s region. (b) Cl 2p region. (c) Pt 4f region.

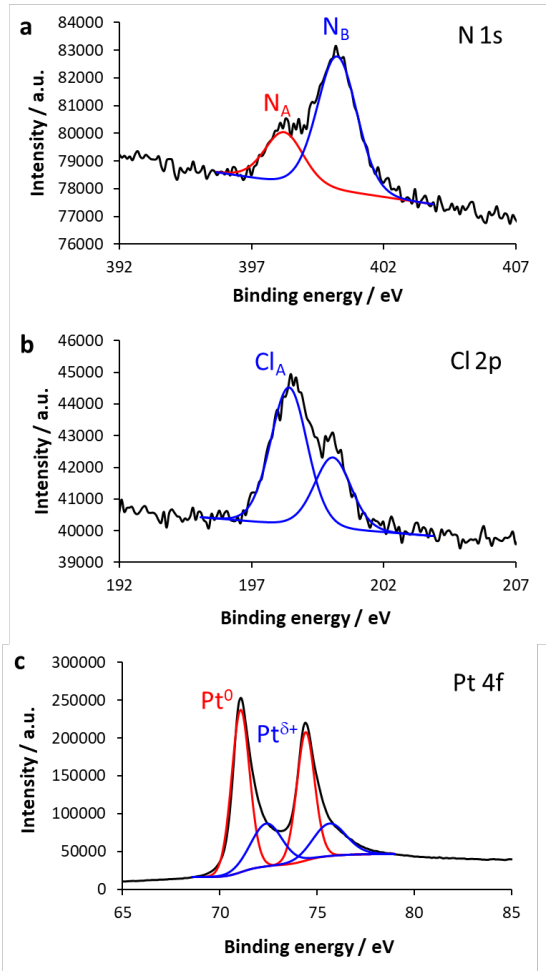


Figure S10. Pt seeds XPS spectra in (a) N 1s region. (b) Cl 2p region. (c) Pt 4f region.

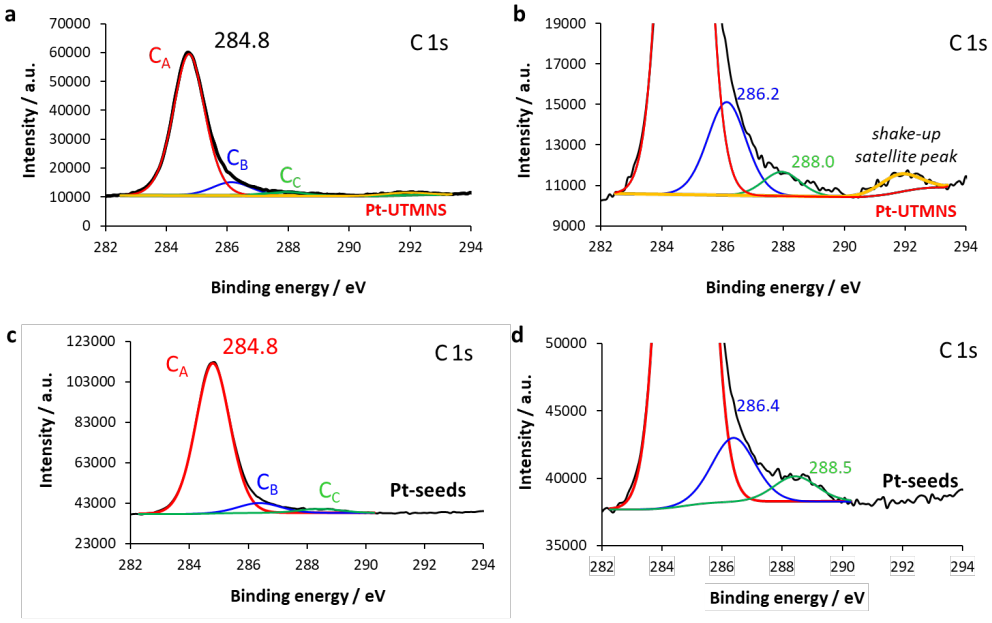


Figure S11. XPS spectra in C 1s region. (a, b) Pt seeds. (c, d) Pt UMNS.

Table S1 Results of fitting of the XPS spectrum in N 1s region of Pt-UMNS and Pt seeds.

Material	N 1s B.E. / eV			FWHM / eV			N_A %	N_B %	N_C %
Pt UMNS	N_A	N_B	N_C	N_A	N_B	N_C			
	398.0	399.6	401.2	1.64	1.69	1.78	13.5	28.5	58.0
Pt seeds	398.2	400.2	-	1.7	1.76	-	26.5	73.5	-

Table S2 Results of fitting of the XPS spectrum in Cl 2p region of Pt UMNS and Pt seeds.

Material	Cl $2p_{3/2}$ B.E. / eV		FWHM / eV		Cl $2p_{1/2}$ B.E. / eV		FWHM / eV		Cl_A %	Cl_B %
Pt UMNS	Cl_A	Cl_B	Cl_A	Cl_B	Cl_A	Cl_B	Cl_A	Cl_B		
	197.7	200.0	1.4	1.2	199.3	201.5	1.4	1.2	83	17
Pt seeds	198.4	-	1.6	-	200.2	-	1.6	-	100	-

Table S3. Results of fitting of the XPS spectrum in C 1s region of Pt UMNS and Pt seeds.

Material	C 1s B.E. / eV			FWHM / eV			C_A %	C_B %	C_C %
Pt UMNS	C_A	C_B	C_C	C_A	C_B	C_C			
	284.8	286.2	288.0	1.22	1.49	1.43	87.5	10	2.5
Pt seeds	284.8	286.4	288.5	1.36	1.68	1.69	90.1	7.1	2.8

Table S4. Results of fitting of the XPS spectrum in Pt 4f region of Pt UMNS and Pt seeds.

Material	Pt $4f_{7/2}$ B.E. / eV			FWHM / eV			Pt $4f_{5/2}$ B.E. / eV			FWHM / eV			Pt^0 %	$Pt^{\delta+}$ %	Pt^{+2} %
	Pt^0	$Pt^{\delta+}$	Pt^{+2}	Pt^0	$Pt^{\delta+}$	Pt^{+2}	Pt^0	Pt^{d+}	Pt^{+2}	Pt^0	Pt^{d+}	Pt^{+2}			
Pt UMNS	70.9	71.9	73.4	1.23	1.66	1.86	74.3	75.2	76.8	1.24	1.62	2.08	61	28	11
Pt seeds	71.1	72.4	-	1.13	1.97	-	74.4	75.6	-	1.12	2.08	-	68	32	0

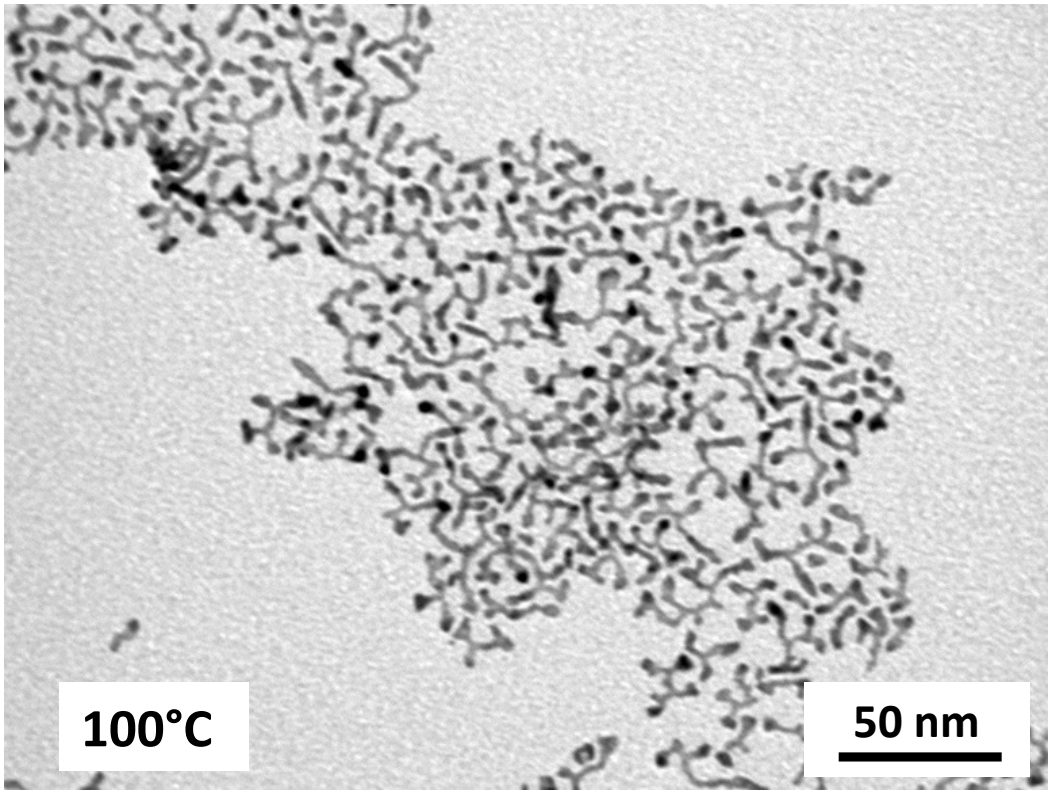


Figure S12. Pt -seeds formed at 100 °C.

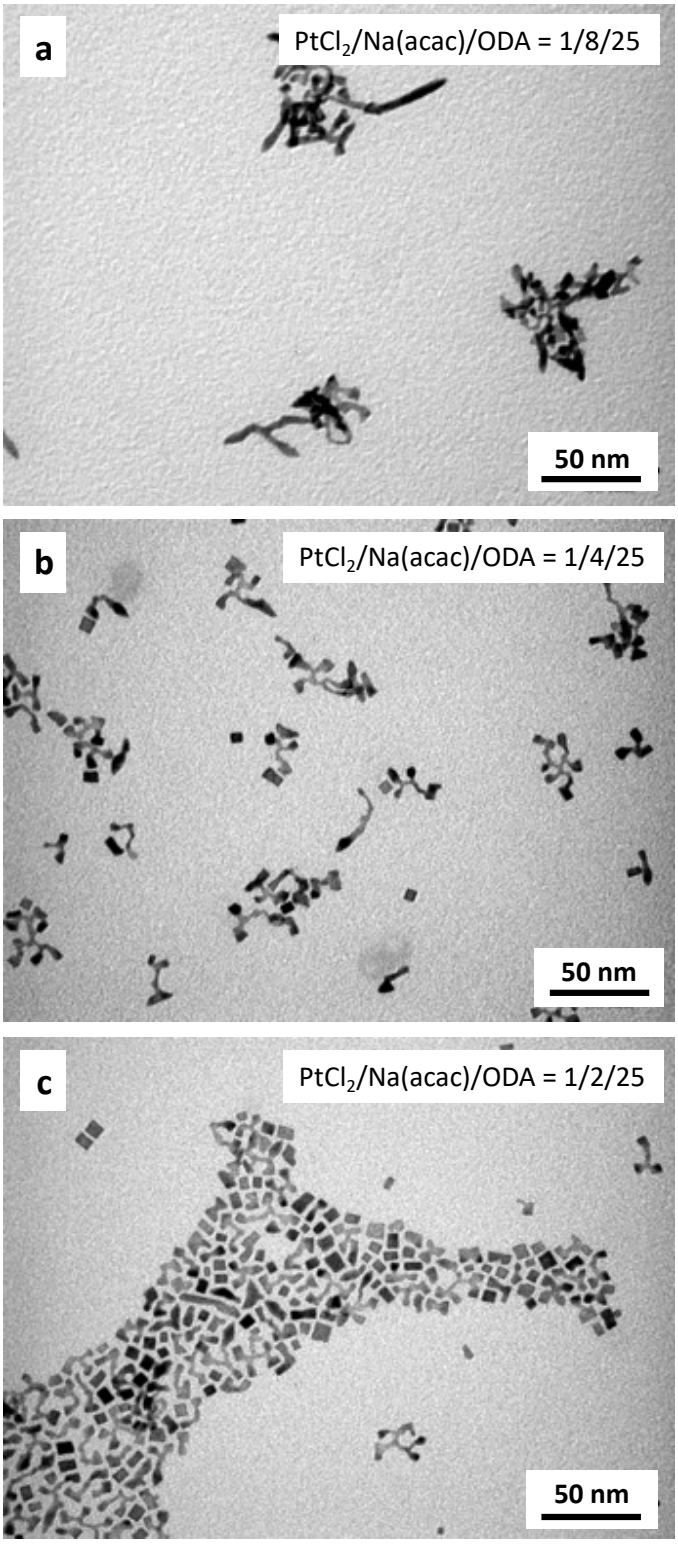


Figure S13. $PtCl_2$/Na(acac)/ODA influence on the formation of dendritic multipods. All the results correspond to 24 h reaction at 20 °C. Pt Cl_2/Na(acac)/ODA: (a) 1/8/25 (reference conditions); (b) 1/4/25; and (c) 1/2/25.

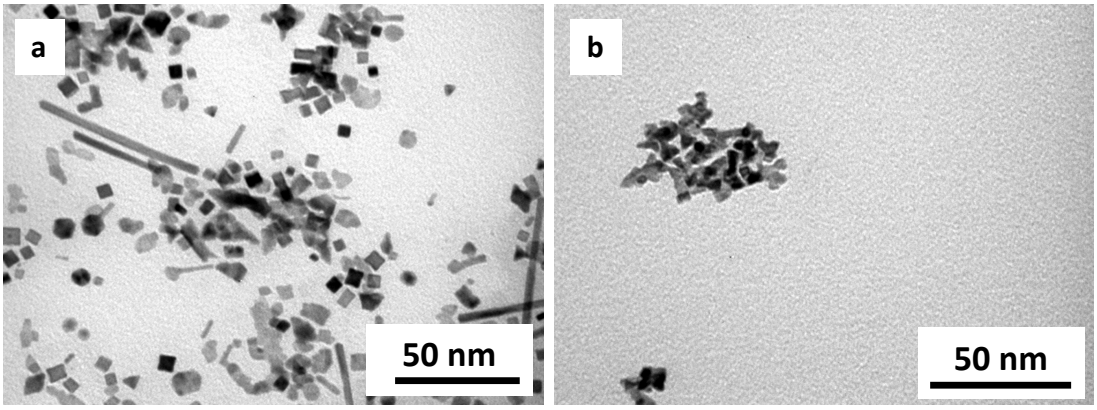


Figure S14. Influence of the reaction temperature. (a) 16 h at 40 °C. (b) 4 days at 10 °C.

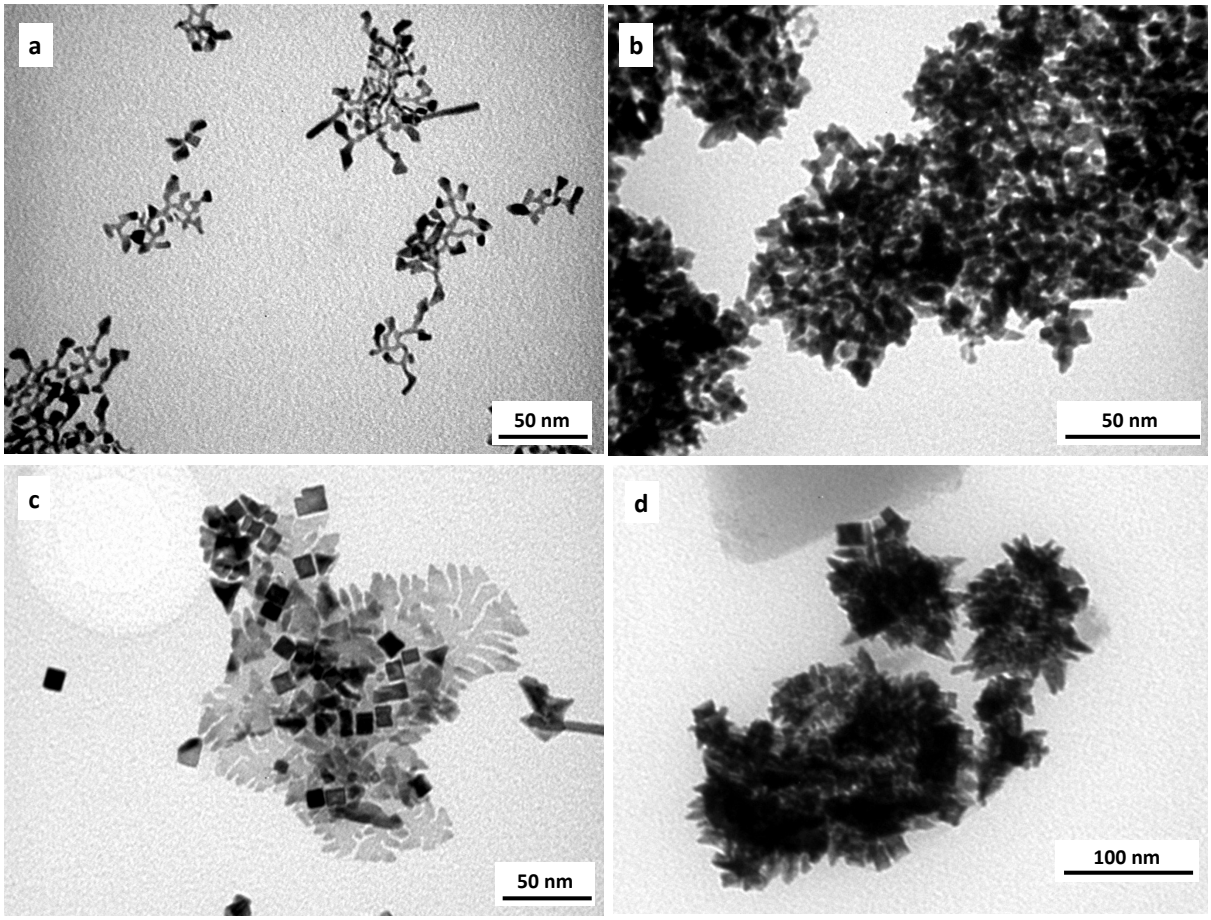


Figure S15. Influence of the amine nature on the Pt seeds and on the Pt UMNS. (a) hexadecylamine. (b) benzylamine. (c) hexadecylamine. (d) benzylamine.

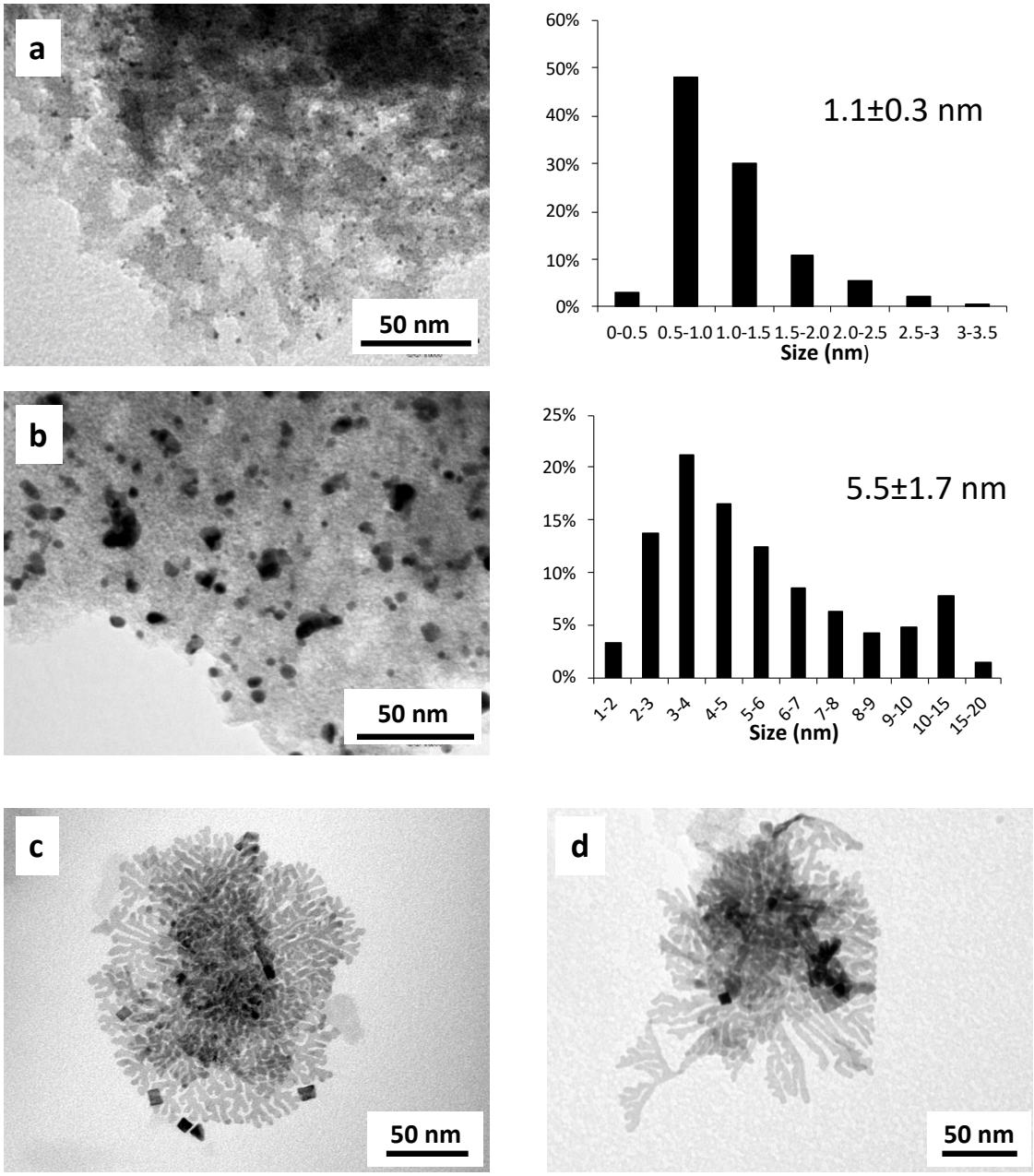
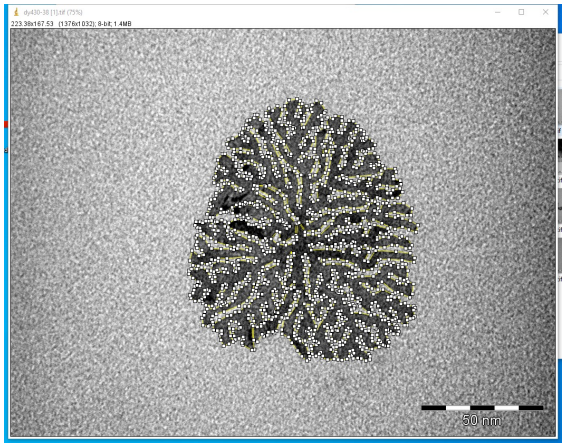


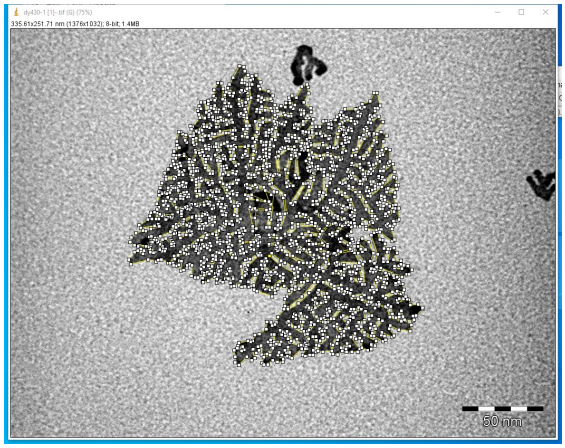
Figure S16. TEM micrographs and particle size distribution: (a) fresh Pt/C; (b) spent Pt/C. TEM micrograph of Pt UMNS: (c) before catalysis; (d) after catalysis.



$S_{(111)}$: 5412 nm^2 ,
$S_{lateral}$: 2947 nm*1 nm=2947 nm^2
S_{Total}=5412*2+2947=13771 nm^2
$S_{lateral}/S_{(111)}$=2947/(5412*2) = 0.272

Volume= 5412*1=5412 nm^3
Mass: 5412* 21.45*10^{-18} mg/nm^3 = 1.16*10^{-13} mg

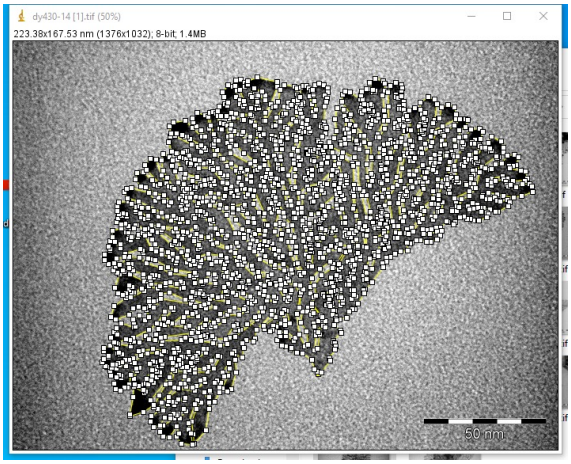
SSA=13771 nm^2/ 1.16*10^{-13} mg = 1.19*10^{17} nm^2/mg
=119 m^2/g



$S_{(111)}$: 14675 nm^2 ,
$S_{lateral}$: 7853 nm*1 nm= 7853 nm^2
S_{Total}=14675*2+7853=37203 nm^2
$S_{lateral}/S_{(111)}$= 7853/(14675*2)= 0.267 %

Volume= 14675*1=14675 nm^3
Mass: 14675 nm^3* 21.45*10^{-18} mg/nm^3 = 3.15*10^{-13} mg

SSA=37203 nm^2/ 3.15*10^{-13} mg = 1.18*10^{17} nm^2/mg
=118 m^2/g



$S_{(111)}$: 10321 nm^2 ,
$S_{lateral}$: 5466 nm*1 nm= 5466 nm^2
S_{Total}= 10321 *2+5466=26108 nm^2
$S_{lateral}/S_{(111)}$= 5466/(10321*2)= 0.266 %

Volume= 10321*1=10321 nm^3
Mass: 10321 nm^3 * 21.45*10^{-18} mg/nm^3 = 2.21*10^{-13} mg

Specific surface area =
26108 nm^2/ 2.21*10^{-13} mg = 1.18*10^{17} nm^2/mg
=118 m^2/g

Figure S17. Screenshots and calculations based on evaluated surface areas and perimeter length. The surface area and the perimeter of the Pt sheet were evaluated by using the polygon tool in ImageJ. 3 discrete UMNS were measured.

The Specific Surface Area (SSA) is given by the following formula

$$SSA = \frac{S_{tot}}{m} = \frac{S_{tot}}{d_{Pt}\,V}$$

with d_{Pt} the density of Pt (21,45 g·cm^{-3}), V the volume of a nanoparticle and S_{tot} the surface area of a nanoparticle. V and S_{tot} were calculated, according to geometrical considerations.

For the commercial catalyst it was assumed that the nanoparticles are spheres with a mean diameter of 1.1 nm.

$S_{tot} = 4\pi r^2 = 3.80$ nm^2

$V = 4/3\pi r^3 = 0.697$ nm^3

SSA = 253 m^2/g

For the UMNS The S_{tot} and the V were evaluated by the following formulas:

$$S_{tot} = 2S_{(111)} + S_{lateral}$$

$$S_{lateral} = P \times L_{thickness}$$

$$V = S_{(111)} \times L_{thickness}$$

Where $S_{(111)}$ is the extended surface of the UMNS, $S_{perimeter}$ is the perimeter surface.

The $S_{lateral}$ can be calculated by the perimeter length (P) and the lateral UMNS mean thickness ($L_{thickness}$) (1 nm, as evaluated by EFTEM and AFM).

The SSA of the UMNS was evaluated to be 118 m^2/g

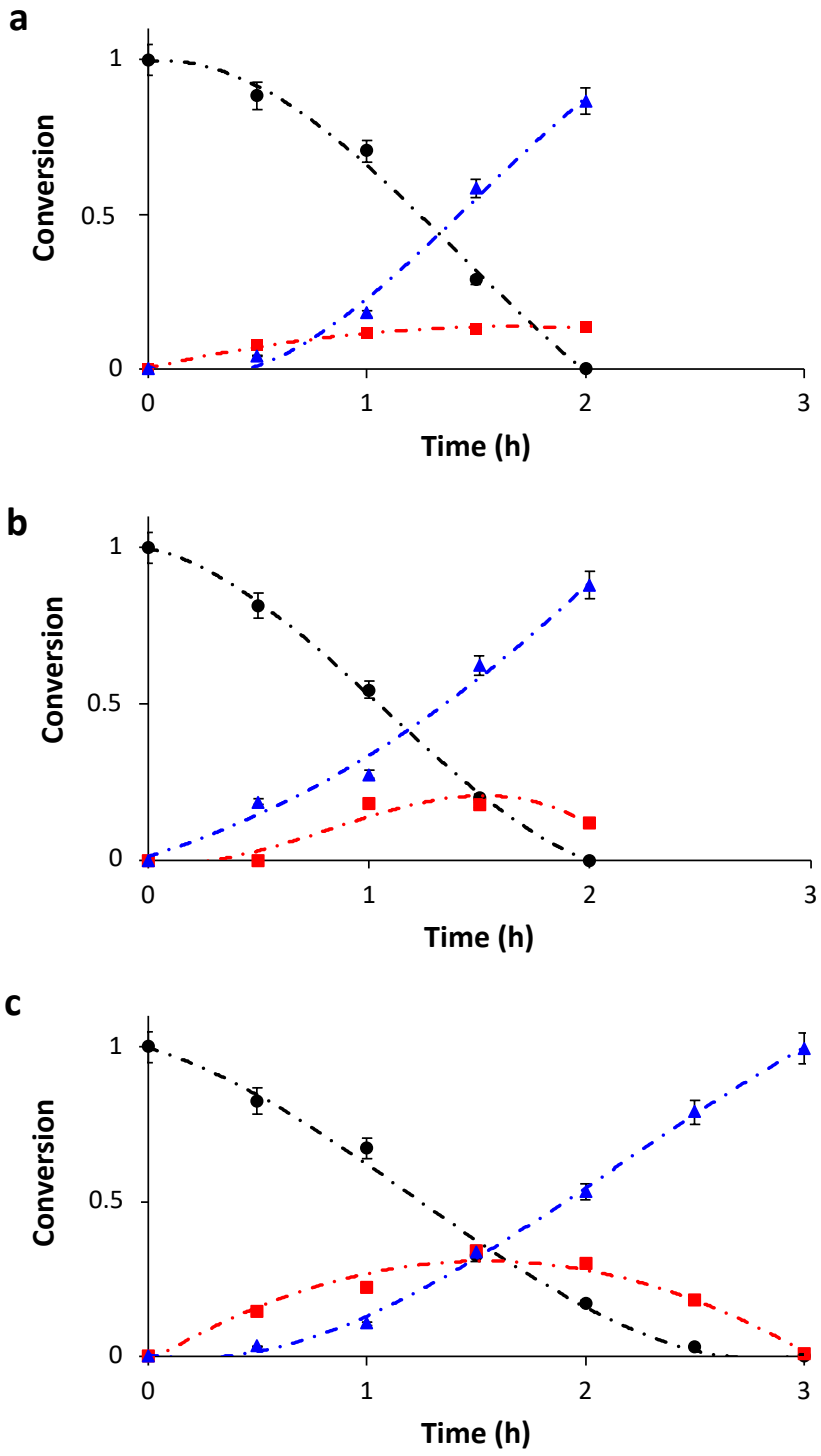


Figure S18. Results of PhA hydrogenation on Pt/C catalysts modified or not with ODA. (a) Pt/C catalyst without additional ODA. (b) Pt-ODA1/C catalyst containing 20%w/w ODA related to Pt. (c) Pt-ODA2/C catalyst containing 20%w/w ODA related to Pt/C, (black circles PhA, red squares ST, and blue triangles EB).

Table S5. Catalytic performances of Pt-based catalysts for selective hydrogenation of phenylacetylene

	Pt NP size (nm)	**T (°C)**	**P_{H2} (bar)**	**TOF (h^{-1})**	**$S_{ST-90\%}$ (%)**	**Ref.**
Pt UMNS	-	25	5	850	77	*This work*
0.5% Pt/γ-Al_2O_3	1.2	30	3,8	75	58	[1]
1%Pt/TiO_2	Single atoms	30	1	294	78	[2]
1,65%Pt/P-SiO_2	1	45	20	396	85	[3]
0,5%Pt/SiO_2	1.5	45	20	2050	52	[3]
2%Pt/CNT	2.6	50	3	1350	67	[4]
1% Pt/TiO_2	2.5	50	3,4	98	88	[5]
1,2%Pt/X-zeolite	1.05	50	5	296	84	[6]
Pt@PVP	2.6	50	1	656	90[a)]	[7]
0.2%Pt@ZSM-22	1,7	65	3	2600	92	[8]

a) Selectivity at 30% conversion.

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