JOURNAL NAME

Platinum nanoclusters made by gas-diffusion electrocrystallization (GDEx) as electrocatalysts for methanol oxidation

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Electronic supplementary information (ESI)

ESI-I Synthesis and characterization of the GDEx-made Pt nanomaterials.

Table S1. Inductively coupled plasma-sector field mass spectrometry instrument settings and data acquisition parameters.

Parameter	
RF power	1300 W
Plasma gas flow rate	13 L min^{-1}
Carrier gas flow rate	0.93 L min^{-1}
Measurement mode	TRA
Nuclide monitored	^{195}Pt
Dwell time	50 µs
Acquisition time	60 s
Nebulizer	MicroMist
Spray chamber	Cyclonic

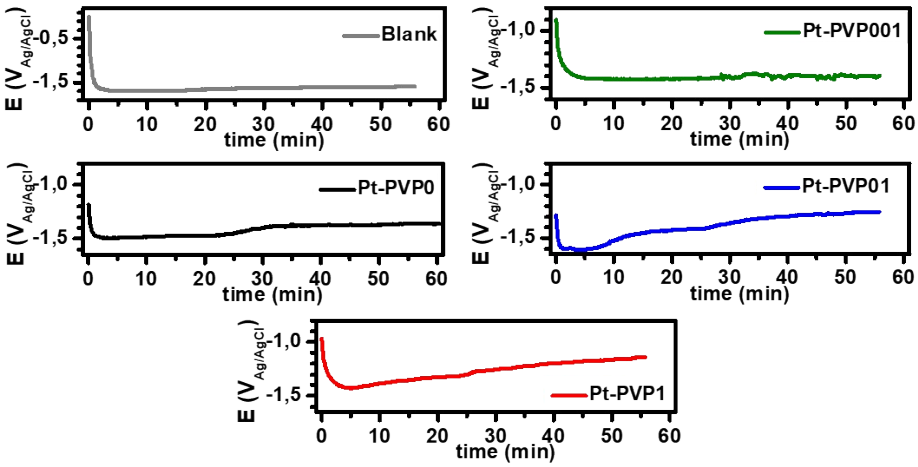

Fig S1. Chronopotentiometric curves of the different experiments performed at -30 mA cm^{-2} at different concentrations of PVP.

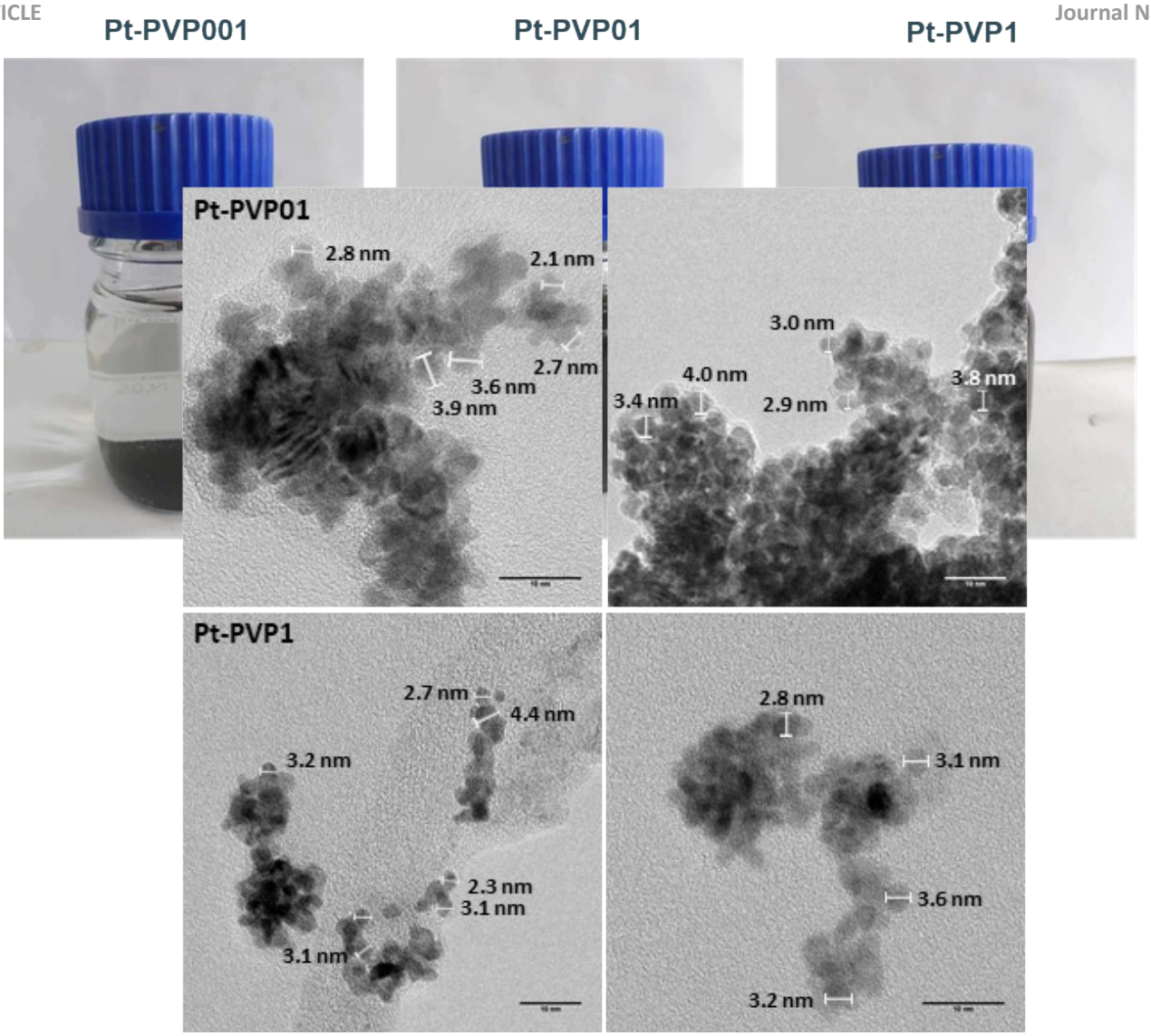

Fig S2. Photographs of the different Pt NCs dispersions right after the synthesis.

Fig S3. TEM images of Pt-PVP-01 and Pt-PVP-1 showing the primary nanoparticles.

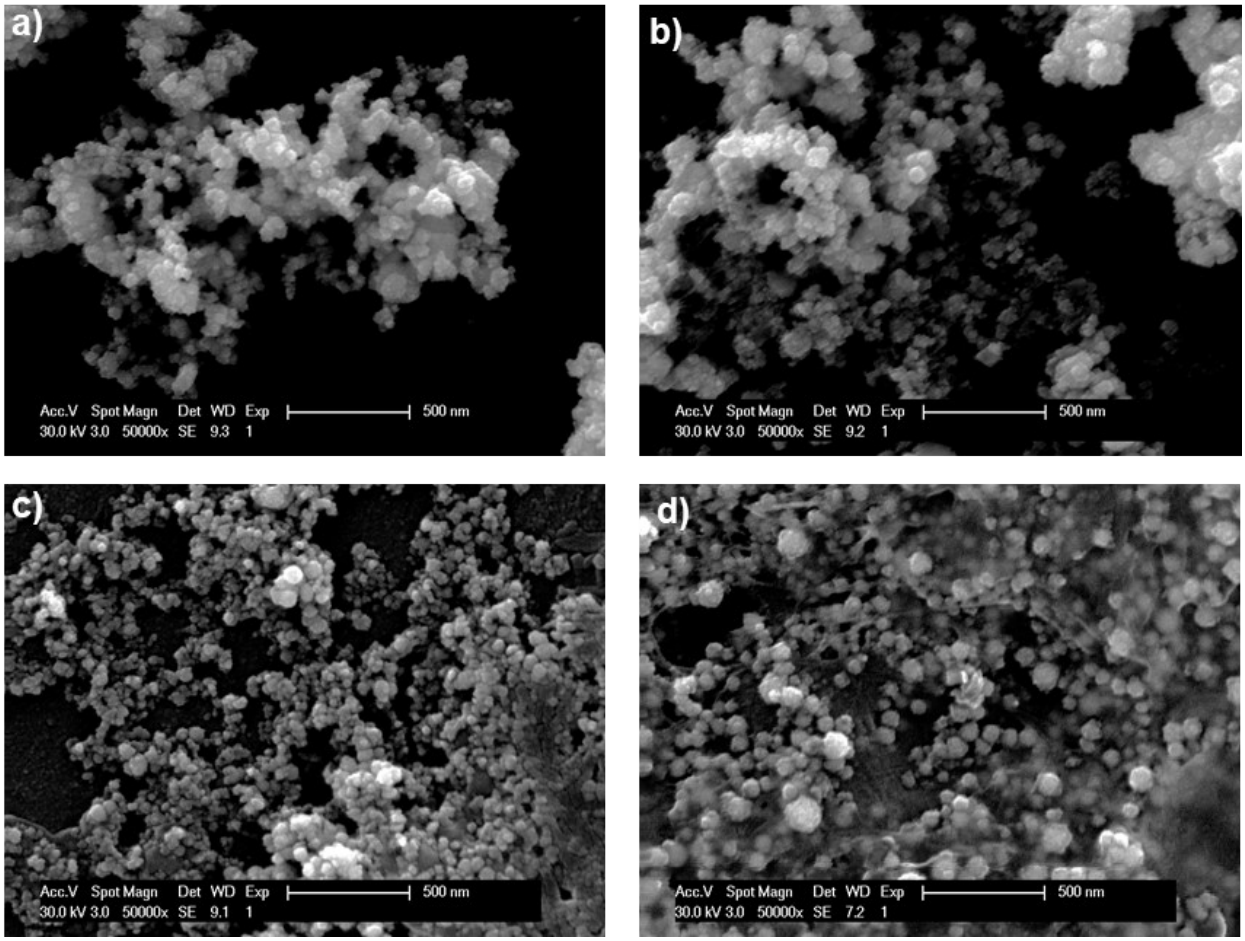

Fig. S4. SEM images of the different Pt NCs. a) Pt-PVP-0, b) Pt-PVP-001, c) Pt-PVP-01, Pt-PVP-1

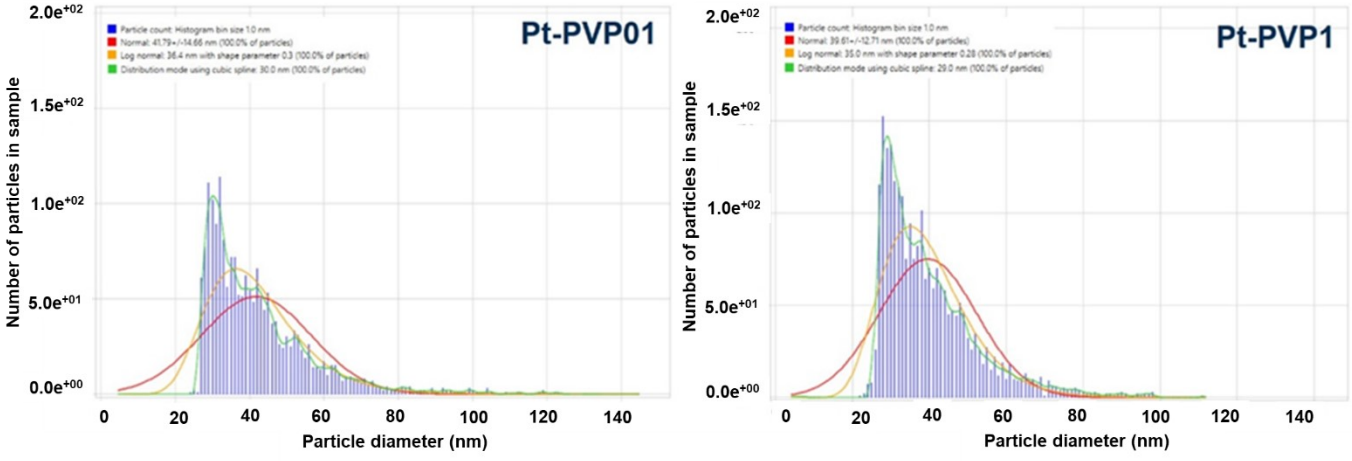

Fig S5. Size distribution histograms of Pt-PVP-01 and Pt-PVP-1 as obtained using spICP-SFMS.

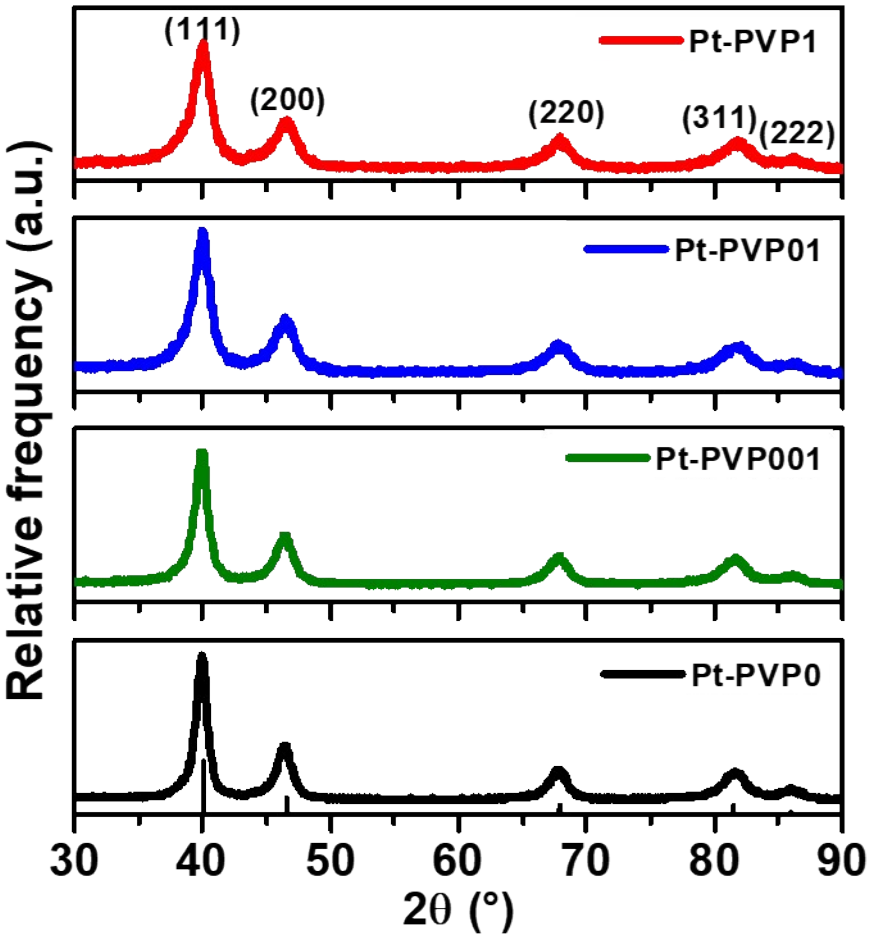

Fig S6. X-ray diffraction pattern of the different Pt NCs.

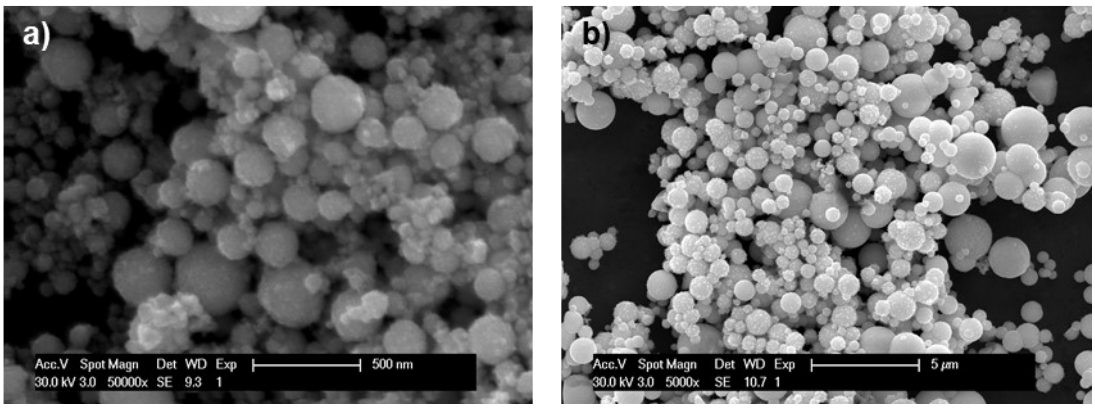

Fig S7. SEM images of Pt products from a) synthesis using GDEx replacing CO_2 with Ar and b) synthesis bubbling H_2. The solution contained 3 mM Pt^{4+}, 0.5 M NaCl and 1.0 g L^{-1} PVP.

ESI-II Surface cleaning of GDEx made Pt NPs

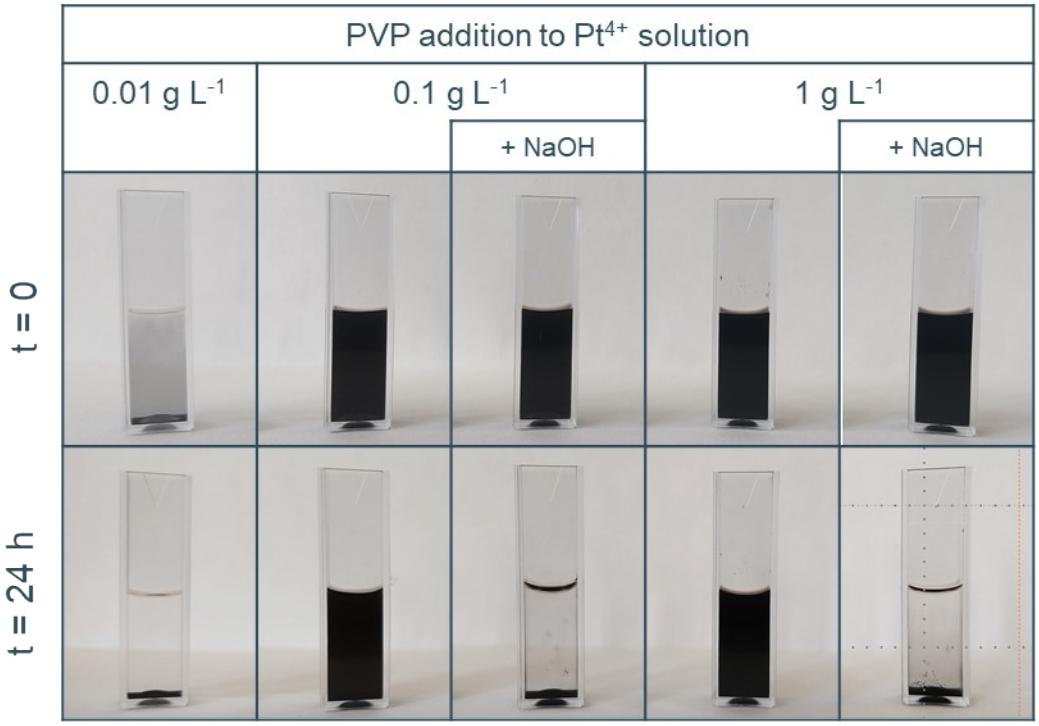

Fig S8. Graphical representation of the NaOH treatment. After the addition of NaOH, the sedimentation of the Pt NCs is observed after 24 h. If NaOH is not added, the NCs suspension of Pt-PVP-01 and Pt-PVP-1 remains stable.

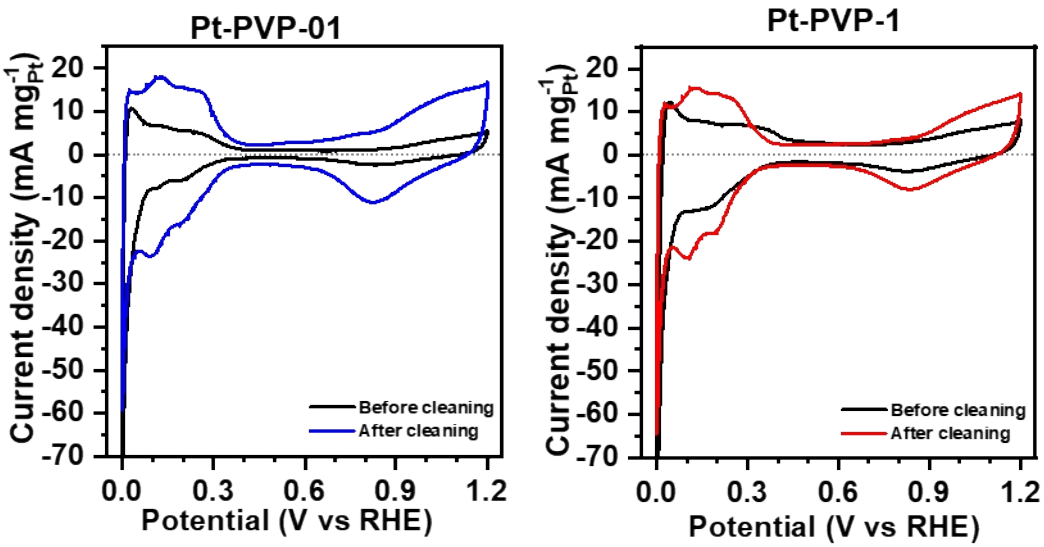

Fig S9. CVs of the Pt NCs in 0.5 M H_2SO_4 at 50 mV s^{-1} before and after the cleaning protocol.

ESI-III Electrocatalytic activity

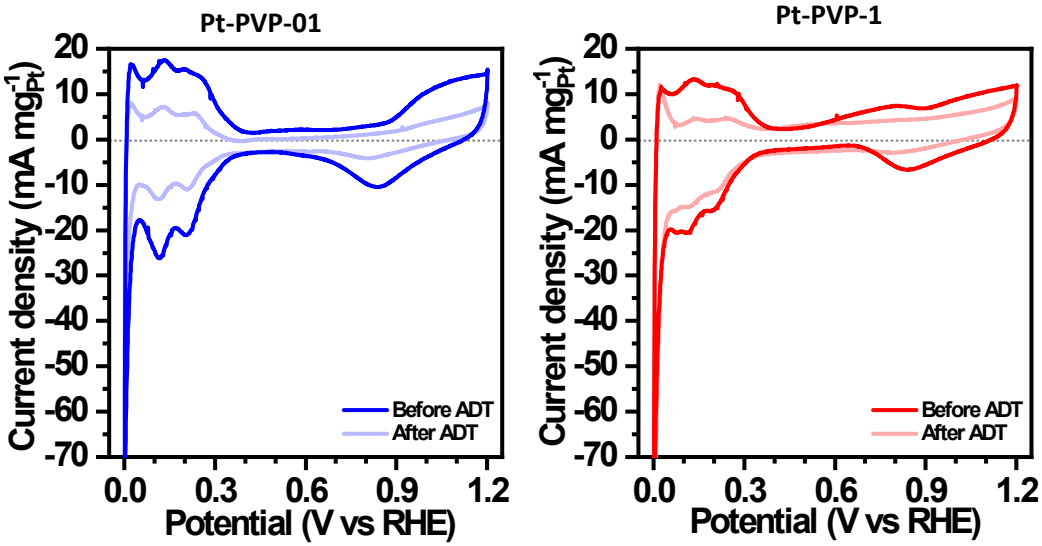

Fig S10. CVs of the Pt NCs in 0.5 M H_2SO_4 at 50 mV s^{-1} before and after the accelerated durability test.

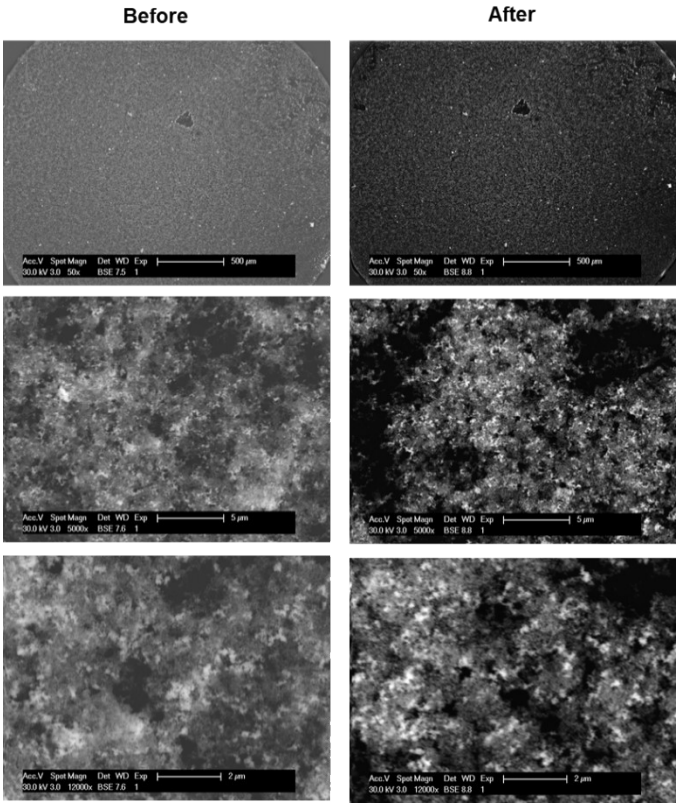

Fig S11. Back-scattered electron SEM images of the surface of the GCE before and after the accelerated stability test of Pt-PVP-01.

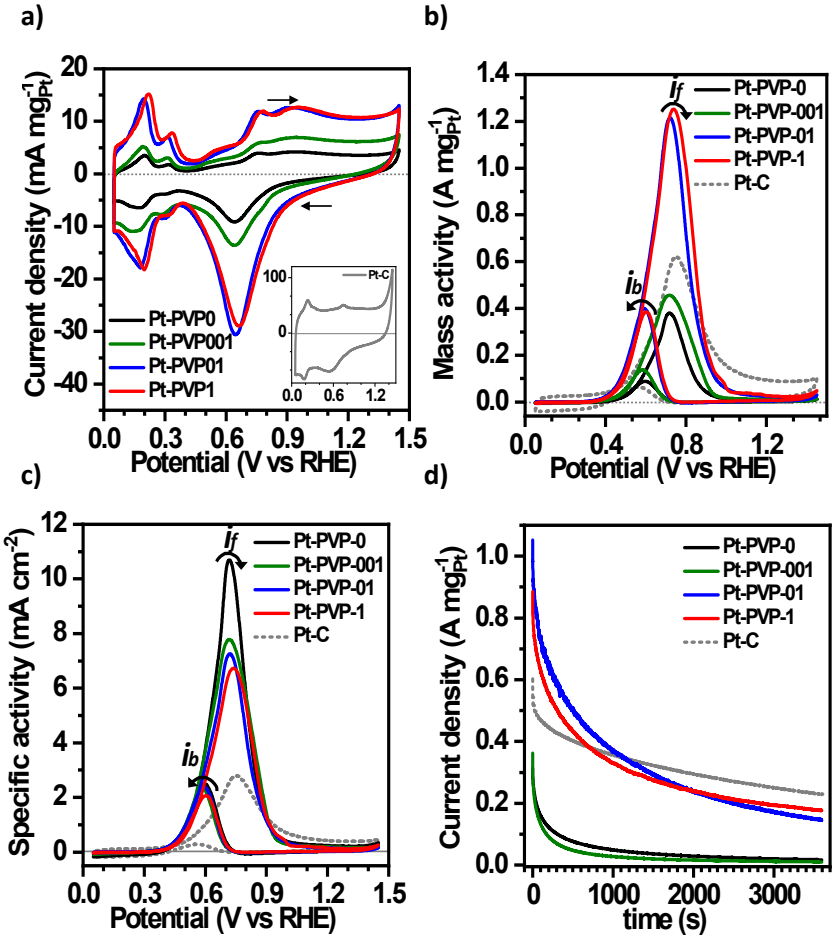

Fig S12. a) CVs of the different Pt NCs in 1.0 M KOH solution at 50 mV s^{-1}, inset: CV of Pt/C. b,c) mass activity and specific activity of the Pt NCs and Pt-C recorded in 1.0 M KOH + 1.0 M MeOH solution at 50 mV s-1. d) Chronoamperograms of the different materials in 1.0 M KOH + 1.0 M MeOH solution at 0.75 V_{RHE}.

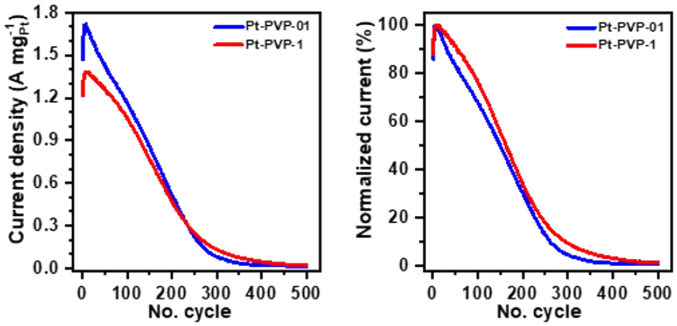

Fig. S13 Accelerated stability test (ADT) of Pt-PVP-01 and Pt-PVP-1 in 0.5 M 1.0 M KOH + 1.0 M MeOH solution at 50 mV. a) MA value at the if, b) normalized data to the highest value.

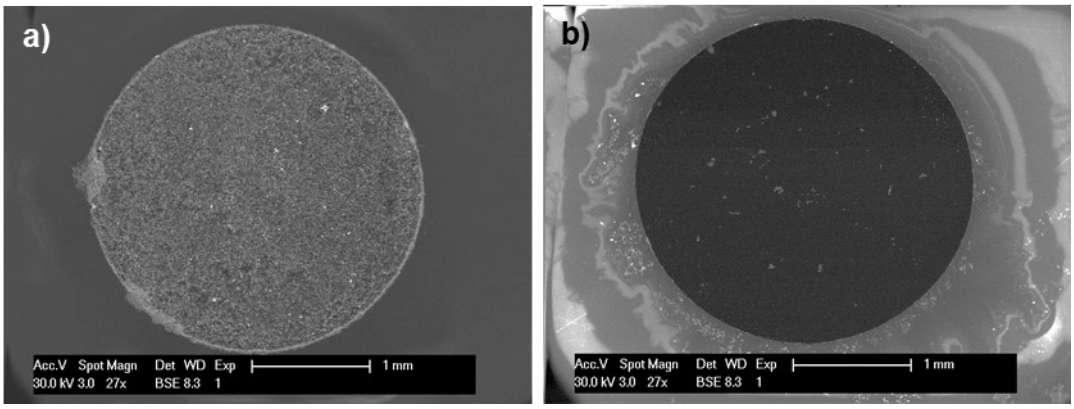

Fig. S14 Back-scattered electron SEM images of the surface of the GCE before and after the accelerated stability test. a) Before, b) after

Table S1. Comparative table of the different unsupported Pt electrocatalysts reported for MeOH oxidation reaction

Material	Media	ECSA ($m^2 g^{-1}$)	Mass activity (mA mg_{Pt}^{-1})	Specific activity (mA cm^{-2})	Ref
Pt-PVP01	0.5 M H_2SO_4 -1.0 M MeOH	33.6	463	1.38	This work
Pt-PVP1	0.5 M H_2SO_4 -1.0 M MeOH	30.3	341	1.12	This work
Pt nanocubes	0.1 M $HClO_4$ -0.2 M MeOH	40.1	330	0.82	[1]
Pt nanoflowers	0.5 M H_2SO_4 /0.5 M MeOH	-	87.7	2.8	[2]
Porous Pt nanotubes	0.5 M H_2SO_4 -1.0 M MeOH	23.9	-	1.62	[3]
High surface area Pt nanotubes	0.5 M H_2SO_4 -1.0 M MeOH	31.54	200	-	[4]
Pt nanowires	0.5 M H_2SO_4 -2.0 M MeOH	71.34	45.50	-	[5]
Pt nanowires	0.5 M H_2SO_4 -2.0 M MeOH	22.8	57.2	-	[6]
Pt NPs assemblies	0.5 M H_2SO_4 -1.0 M MeOH	51.5	239	-	[7]
Dendritic Pt NPs	0.5 M H_2SO_4 -0.5 M MeOH	27.8	-	0.85	[8]
Dendritic Pt NPs	0.5 M H_2SO_4 -0.5 M MeOH	37.4	118		[9]
Spiny-porous Pt nanotubes	0.5 M H_2SO_4 -1.0 M MeOH	46.5	260	0.55	[10]
Pt-PVP01	1.0 M KOH -1.0 M MeOH	47.0	311	0.66	This work
Pt-PVP1	1.0 M KOH -1.0 M MeOH	41.1	514	1.25	This work
Pt porous nanotubes	1.0 M KOH -1.0 M MeOH	47.2	2330	4.94	[11]

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