# Supporting Information

# Tailored concave platinum nanocrystals for the selective electro-oxidation of formic acid

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# Physical characterization

The FE-SEM images were acquired using a TESCAN Mira 3 field emission scanning electron microscope (FE-SEM) at an accelerating voltage of 30 kV, and the average particle size of the prepared Pt-NCs was determined using ImageJ software. For high-resolution transmission electron microscopy (HR-TEM) analysis and imaging, a well-dispersed Pt-NCs catalyst sample was prepared by sonicating the 1 mg catalyst with ethanol. A well-dispersed mixture was drop-coated on the 200-mesh carbon-coated copper grid and dried overnight, and the images from low to high resolutions were obtained from the FEI, Talos F200S instrument operated at an accelerated voltage of 200 kV. HR-TEM image analysis is carried out using Gatan software. p-XRD pattern for Pt-NCs was recorded on Bruker, D8 Advance model, having X-ray source CuKα with λ=1.546 Å and Lynx Eye & Scintillation Counter as a detector. The p-XRD patterns were collected in continuous scanning mode (scan time: 20 min) in the 2θ range of 20 to 80°. X-ray photoelectron spectroscopy analysis of the prepared samples was done on a Thermo-scientific made ESCALAB 250xi BASE SYSTEM WITH UPS AND XPS IMAGE MAPPING model. Fourier-transform infrared (FT-IR) spectra were recorded using an IRSpirit instrument from Shimadzu Pvt. Ltd.

# Supplementary Figures:

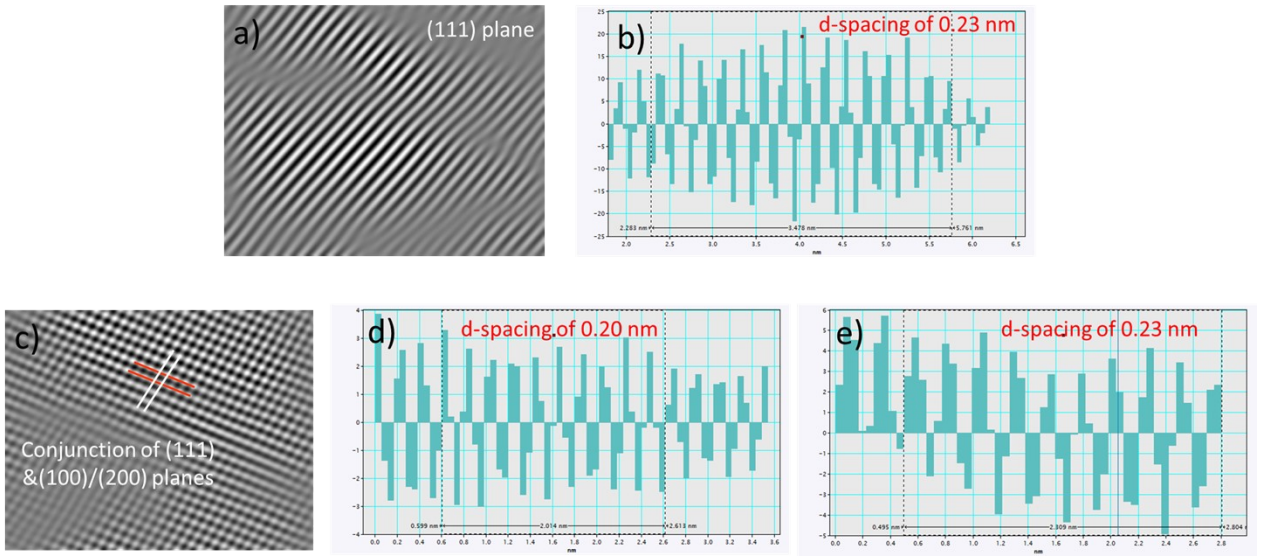


**Fig. S1** (a, b) IFFT image and d-spacing profile for (111) plane, and (c-e) IFFT image and d-spacing profile for (111) & (100)/ (200) plane of Pt-NCs.

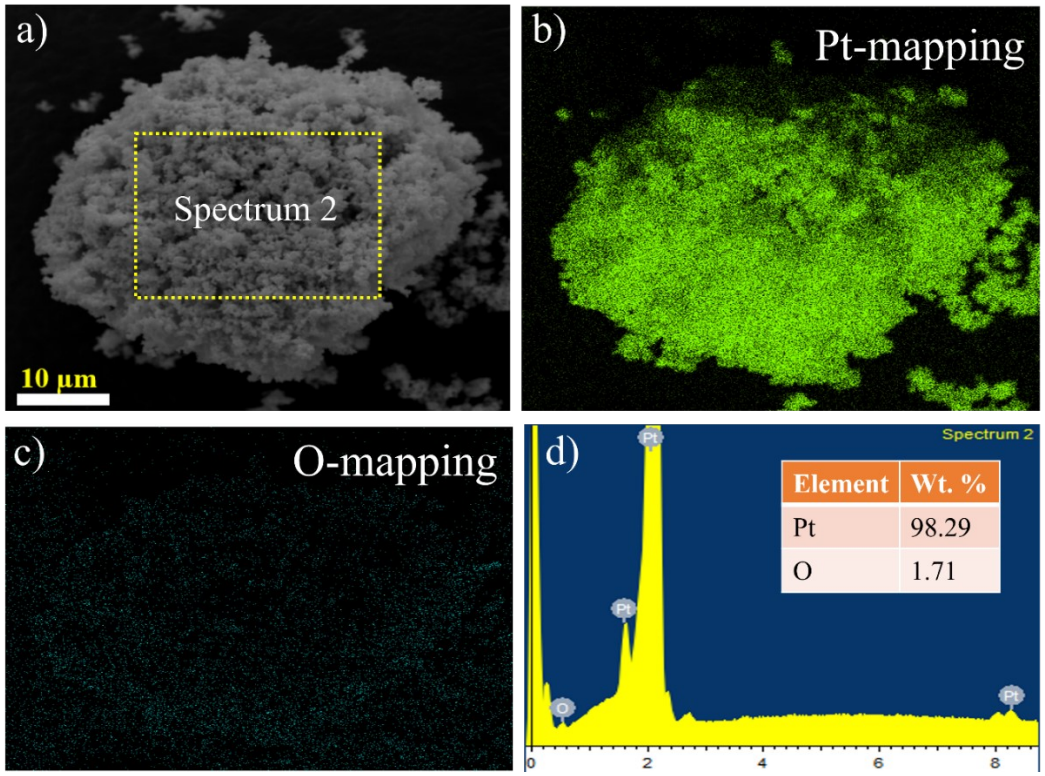


**Fig. S2** (a) EDX spectra of Pt-NCs, Elemental mapping of (b) Pt, (c) O, and (d) Elemental distribution for Pt-NCs, inset: weight percentage of elements.

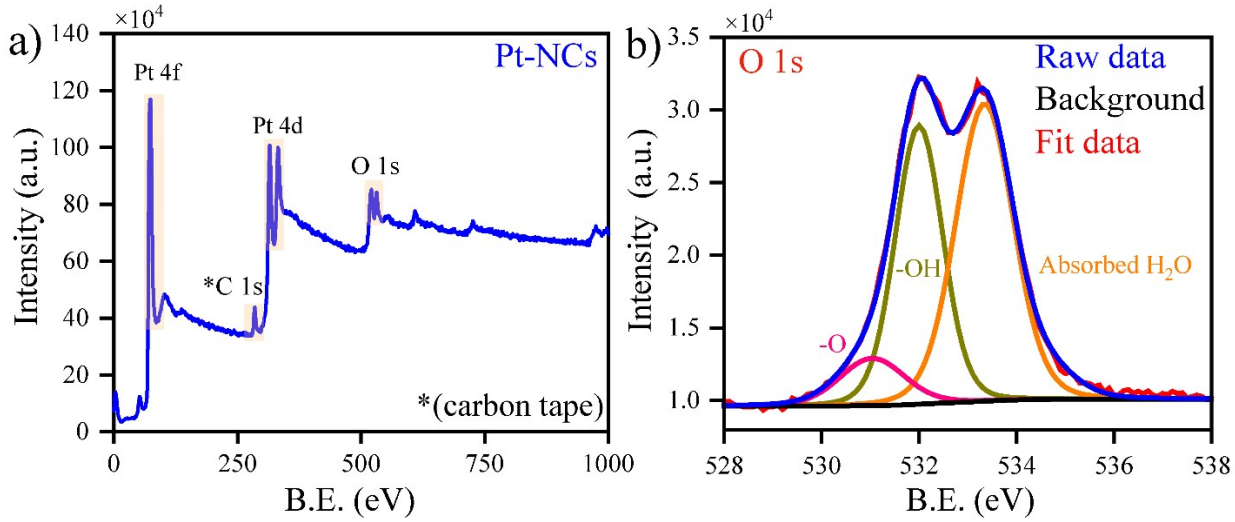


**Fig. S3** Pt-NCs (a) survey spectra and (b) deconvoluted O 1s spectra.

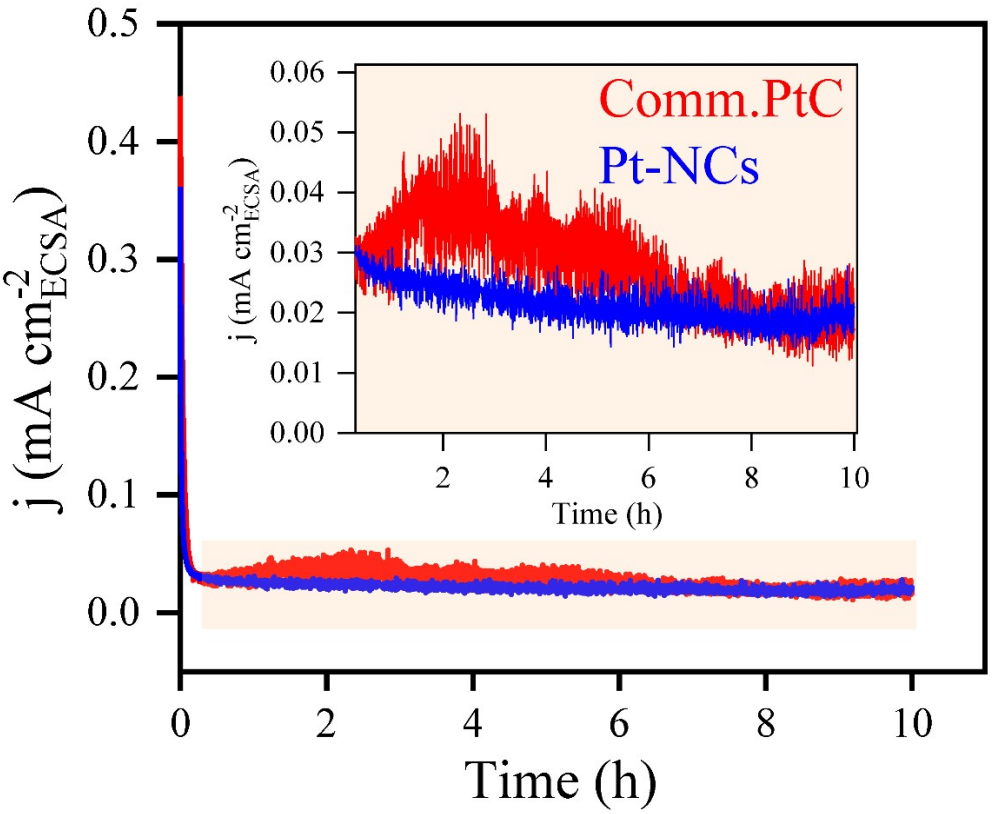


**Fig. S4** Comparative chronoamperometric stability studies for Comm. Pt/C and Pt-NCs, inset: enlarged view of highlighted portion. (Conditions: Electrolyte: 0.1 M HCOOH in 0.1 M $HClO_4$; Counter electrode: graphite rod; Reference electrode: Ag/AgCl; RPM: 400; Applied potential: 0.96 V vs RHE)

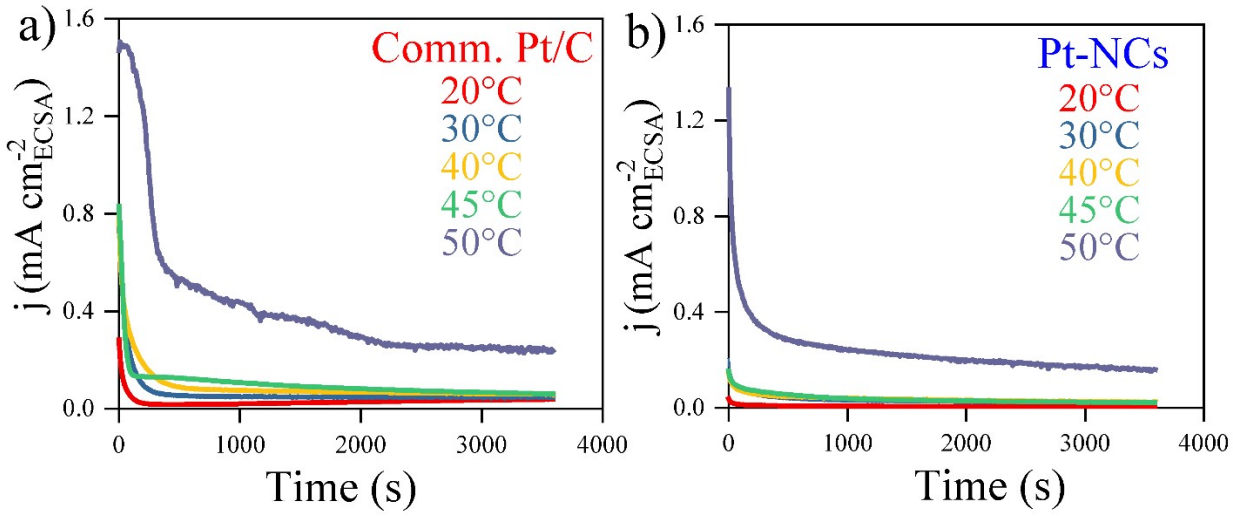


**Fig. S5** (a-b) Comparative CA study at 20, 30, 40, 45 and 50 °C temperatures for Comm. Pt/C and Pt-NCs, respectively. (Conditions: Electrolyte: 0.1M HCOOH in 0.1 M $HClO_4$; Counter electrode: graphite rod; Reference electrode: Ag/AgCl; RPM: 400; Applied potential: 0.96 V vs RHE)

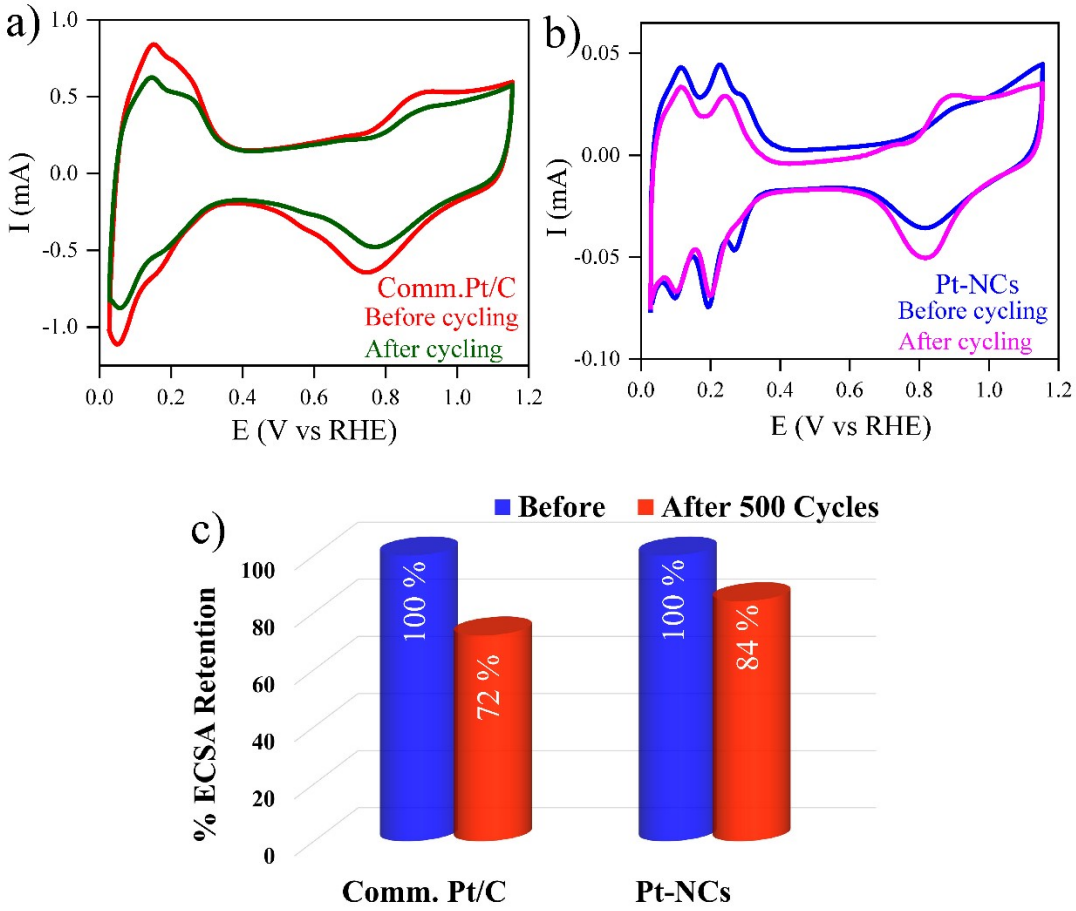


**Fig. S6** Comparative CVs of Comm. Pt/C and Pt-NCs before and after 500 cycles of FAO in 0.1 M $HClO_4$+0.1 M HCOOH, (a and b) recorded in 0.1 M $HClO_4$, and (c) % ECSA retention calculated from the data of "a and b". [CVs are recorded with a scan rate of 50 mV $s^{-1}$, and the electrolyte is purged with nitrogen prior to use]

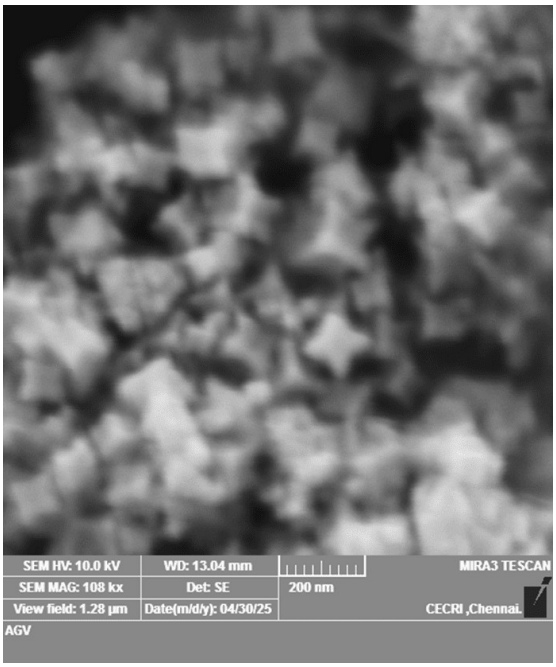


**Fig. S7** Post-stability FE-SEM micrograph of Pt-NCs

**Table S1:** Literature report comparison of formic acid oxidation Pt-based catalysts and prepared Pt-NCs.

| Sl. No | Catalyst name | Synthesis method | Electrolyte | $I_a/I_b$ | $I_a/I_c$ | Reference |
|---|---|---|---|---|---|---|
| **1** | **Pt-NCs** | **Solvothermal** | **0.1 M HCOOH + 0.1 M $HClO_4$** | **1.14** | **0.47** | **This work** |
| **2** | **Comm. Pt/C** | **Solvothermal** | **0.1 M HCOOH + 0.1 M $HClO_4$** | **0.47** | **0.45** | **This work** |
| 3 | $Pt_1Co_1$ | Microwave | 0.5 M HCOOH + 0.5 M $H_2SO_4$ | 0.66 | 0.65 | *ACS Catal.*, 2024., **14**, 18333−18344 |
| 4 | $Pt_1Co_3$ | Microwave | 0.5 M HCOOH + | 0.65 | 0.65 | *ACS Catal.*, 2024., **14**, 18333−18344 |

| | | | | | | |
|---|---|---|---|---|---|---|
| | | | 0.5 M $H_2SO_4$ | | | |
| 5 | $Pt_{74}Cu_{26}$/ concave NPs | Green chemical approach | 0.5 M HCOOH + 0.1 M $HClO_4$. | 0. 38 | - | *J. Mater. Chem*., 2012, **22**, 4780-4789. |
| 6 | $Ir_{50}Pt_{50}$/Au | Thermolytic process | 0.1 M HCOOH + 0.1 M $HClO_4$ | - | 1.84 | *J. Mater. Chem.,* 2011, **21**, 9169–9178. |
| 7 | $Pt_{10.9}Au_{0.2}$ $Ni_{88.9}$/C | Chemical reduction | 0.5 M HCOOH + 0.1 M $HClO_4$ | 0.34 | - | *Int. J. Hydrogen. Energy*., 2020, **45**, 22893–22905. |
| 8 | Mn/Pt/GC | Electro-deposition | 0.3 M HCOOH | 3.13 | 0.50 | *J. Chem.,* 2022, **2022**, 3762138. |
| 9 | PtPd/GC | Co-Electro-deposition | 0.3 M HCOOH | 7.33 | 0.32 | *Energy Rep.,* 2022, **8**, 560–564. |
| 10 | Pt/MWCNTs-GC | Electro-deposition | 0.3 M HCOOH | 7.5 | 0.45 | *Int. J. Electrochem. Sci*., 2019, **14**, 8267–8275. |
| 11 | a-FeOx/Pt | Electro-deposition | 0.3 M HCOOH | 17.4 | 0.70 | *J. Nanotechnol*., 2018, **2018**, 4657040. |
| 12 | $Au_{23}/Pt_{63}Co_{14}$ HNWs/C | Two-step chemical synthesis | 0.5 M HCOOH + 0.1 M $HClO_4$ | 3.7 | - | *Fundam. Res*., 2021,**1**, 453 460. |
| 13 | FeOOH/Pt/GC | Sequential electro-deposition | 0.3 M HCOOH | 5.0 | 0.35 | *Int.J. Hydrogen. Energy*, 2022, **47**, 264–275. |
| 14 | m-PtTeNT/C | Solvothermal | 0.5 M HCOOH + 0.5 M $H_2SO_4$ | 1.88 | - | *J. Am. Chem. Soc.,* 2023, **145**, 15393–15404. |

| | | | | | | |
|---|---|---|---|---|---|---|
| 15 | $Pt_2$–$PtTe_2$ HJNSAs | One-pot-chemical method | 0.5 M HCOOH + 0.5M $H_2SO_4$ | 1.51 | - | *ACS Nano.,* 2024, **18**, 10008–10018. |
| 16 | 100 nm Pt nanotubules | Template wetting | 0.25 M HCOOH + 0.5M $H_2SO_4$ | - | 0.27 | *Int. J. Electrochem.,* 2013, **1**, 42451. |
| 17 | Pt/RGO-600 | Chemical co-reduction | 0.5 M HCOOH + 0.5 M $H_2SO_4$ | 0.79 | - | *J. Mater. Chem. A*, 2015, **3**, 12000–12004. |
| 18 | AgPt Nanoparticles | Hydrothermal | 0.5 M $H_2SO_4$ + 1 M HCOOH | 2.55 | - | *Nano Res*., 2018, **11**, 499–510. |
| 19 | AgPt Nanowires | Hydrothermal | 0.5 M $H_2SO_4$ + 1 M HCOOH | 1.9 | - | *Nano Res.,* 2018,**11**, 499–510. |

**-** *Indicates the values are not mentioned in the particular literature.*