Electronic Supplementary Material (ESI) for Nanoscale.

Supplementary Notes

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Fabrication process steps

The fabrication process of the multilayer graphene electrode, as shown in Fig. 1 (a), starts with 300 nm thermal wet oxide growth on the front side of a silicon (Si) wafer at 1000 ◦C. Next, 50 nm molybdenum (Mo) is sputter-deposited at 50 ◦C on the oxide layer. The Mo layer is then patterned and etched to serve as the catalyst layer for the following graphene growth. Mo etch is performed using an inductively coupled plasma (ICP) etcher with 50 W RF power, 500 W ICP power, 5 mTorr pressure, 25 ◦C temperature, and 30 and 5 sccm Cl_2 and O_2 gas flows, respectively. Then, graphene is selectively grown on pre-patterned Mo using a chemical vapor deposition (CVD) process (using an Aixtron Black Magic Pro tool) at temperatures of 935 ◦C, 25 mbar pressure, and using 960, 40, and 25 sccm of Ar, H_2, and CH_4 gas flows, respectively, and cooled to room temperature under an Ar atmosphere.
The growth time is 20 minutes which results in 7 graphene layers as shown in [11]

Then, an aluminum (Al) / titanium (Ti) stack is sputtered and photolithographically patterned to allow for wire bonding on the contact pads. The Al/Ti layer is then etched in a 0.55% concentration of hydrofluoric acid (HF) to remove this layer from the whole wafer except the contact pads. Next, the photoresist (PR) is spin-coated as an insulation layer and patterned on the electrodes and contact pads. Finally, Mo underneath the graphene electrodes is etched using wet etching in hydrogen peroxide (H_2O_2), leaving the graphene in the exact same location as defined by the catalyst. This is shown in the cross-sectional view of the graphene electrode before and after etching Mo in 1(a).

Nanoparticle printing setting

Table S1. Nanoparticle printing setting

Nominal NP surface density (%)	Calculated surface density (%)	Printing speed (mm/s)	Line width (µm)	Voltage (kV)	Current (mA)	Carrier gas flow (L/min)	Nozzle height (mm)	Nozzle diameter (mm)
15	17.55	137.0	526	1	3	N_2 (1.5)	0.5	0.35
30	30.30	67.0	554					
40	39.90	38.3	637					

For the ease of comparison, 17.55% NP surface density was considered 15% in the text.

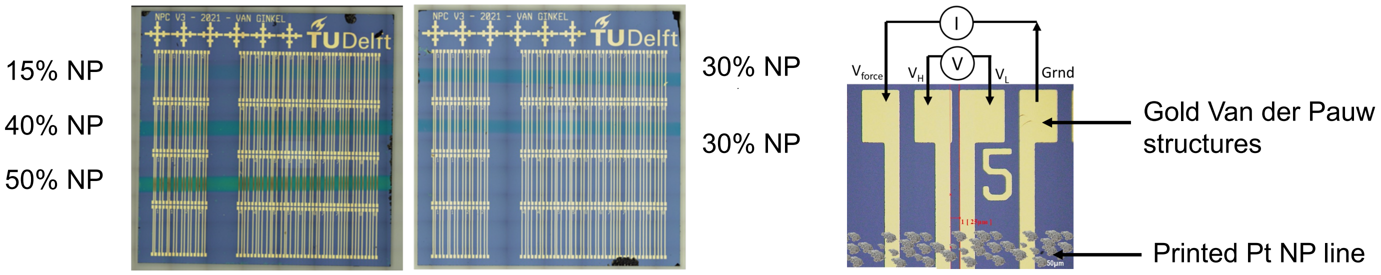
Conductivity measurement

Since the Pt NPs were printed as a line that goes from the insulating layer to the exposed electrode, the printed line may create a conducting path. To better understand this behaviour, a four-point probe measurement test was performed. A line pattern was printed over vertical metal tracks (100 nm gold with 10 nm chromium) on the samples. The measurement was performed by passing a current through two outer probes and measuring the voltage between two inner probes as shown in Figure S1 (a). The test was conducted twice for each printed line (with surface densities of 15, 30, 40, and 50%) at different locations. However, the distance between the inner probes was kept constant at 25 μm. The measurement was conducted from -500 mV to 500 mV with 8 mV steps.

Out of the eight measurement attempts (2 tests for each line sample), only 2 samples showed a current above the noise floor of the instrument. Hence, there is a conducting path along those measured areas. Two tests for the print sample of 50% NP show a conductive circuit. Presented in Figure S1(b) are the current-voltage curves measured for these closed circuits. The sheet resistance for these printed lines is calculated based on Equation (1) and are shown in Figure S1(b). R_{sh1} and R_{sh2} represent the sheet resistance of the printed line for the two measurement tests and R_{sh_avg} is the average of the sheet resistance from these two measurements. Additionally, the 40% NP line did not have any current flowing on both tests, and the height difference between the exposed graphene electrode and the insulating layer (3 μm) on the final electrode samples likely severs any connecting path for print speeds of 40% NP and lower. Although, this is likely not the case for the 50% NP printed line with stable linear current-voltage characteristic curves. Therefore, the electrodes with 50% NP were removed from further characterization.

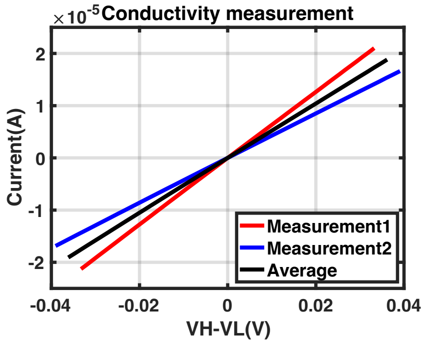
$$\boldsymbol{R_{sh}} = \frac{\pi}{Ln2}\frac{V_H - V_L}{I_{force}} \qquad \text{Equation (1)}$$

(a)



(b)

Test result of 50% NP



$$R_{sh1} = 7126.2 \ \pm 86.2\ \Omega$$
$$R_{sh2} = 10576 \ \pm 133.2\ \Omega$$
$$R_{sh\_avg} = 8650.4 \ \pm 95.6\ \Omega$$

Figure S1. Conductivity measurement (a) Samples with Pt NP lines with the corresponding printing speed printed over gold Van der Pauw structures for the four-point probe measurement, (b) Results of the four-point probe measurements of 50% NP surface density printed lines.

Raman spectroscopy, optical transmittance, and surface roughness measurements:

As explained in the manuscript, Raman spectroscopy, surface roughness, and optical transmittance measurements are performed for the electrodes. The details of each measurement can be found below:

Raman spectroscopy
Raman spectroscopy is used to investigate the effect of NP printing on the graphene lattice structure. For the Raman characterization, a Renishaw inVia system with a red HeNe laser of 633 nm is used. Raman spectroscopy is performed before and after NP printing on the electrode surface.

Surface roughness
The NP surface density can only indicate the 2D distribution of the NPs. To indicate a 3D NP distribution over the electrode surface, surface roughness measurements are performed. A high surface roughness has been shown to increase the CSC due to an increase in the electrochemical surface area of the electrode 35. The surface topography of the Pt NPs printed with multiple surface densities is investigated through atomic force microscopy (AFM; Ntegra). Samples are prepared by printing Pt NP lines on a silicon die. The topography of these samples is tested at a frequency of 0.50 Hz in semi-contact mode with a scan size of 10 µm by 10 µm. This measurement is performed 5 times for each sample at different locations throughout the printed NP lines but as far as possible from the line edges. The AFM data is further processed using Gwyddion applying polynomial correction of the background.

Optical transmittance measurements
The optical transparency of different NP surface densities is assessed for wavelengths in the range of 300 nm to 900 nm (using a Perkin Elmer Lambda 950 UV/Vis spectrophotometer, Waltham, Massachusetts). NPs are printed directly on glass slides (1 sample per surface density). To create a sufficiently large area covered with NPs for this measurement, the printer's nozzle follows a laddered path, i.e., a line is printed along the x-direction followed by a step in the y-direction. Since the line width for each NP density is determined through the method discussed previously, a logical step at the y-direction is considered for each NP density to minimize the chance of overlapping with the previous line.

Atomic force microscopy (AFM)

Table S2. RMS and mean surface roughness

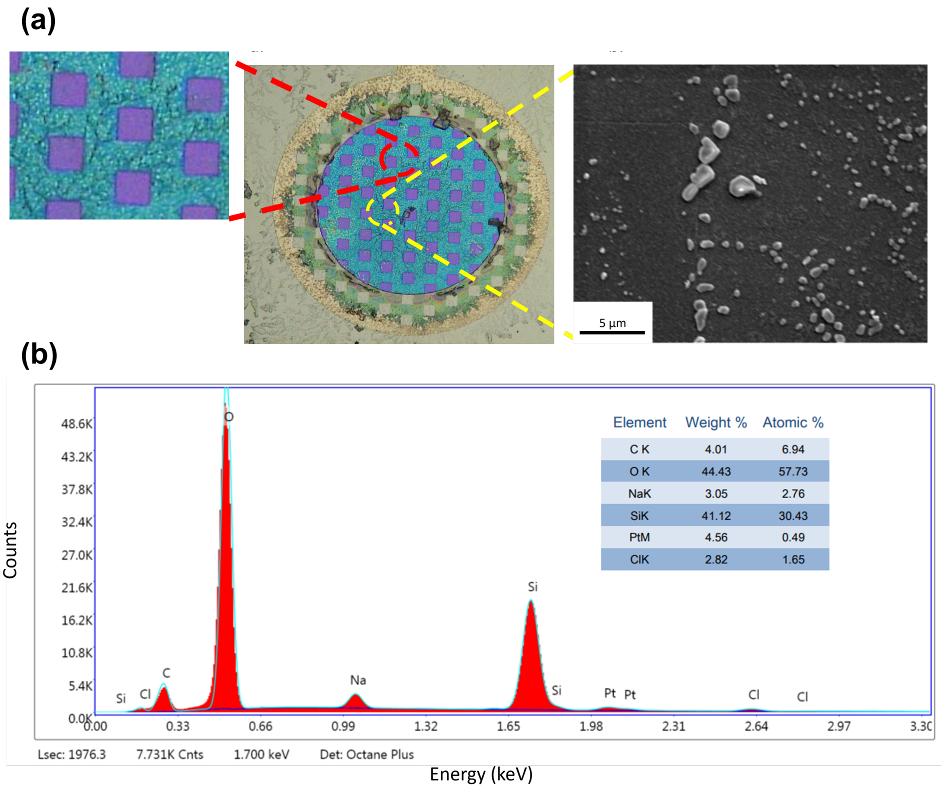
Nominal NP surface density (%)	RMS surface roughness (nm)	Mean surface roughness (nm)
15	9.00 ± 0.87	7.11 ± 0.72
30	9.41 ± 1.37	6.96 ± 0.20
40	14.66 ± 7.31	12.03 ± 6.36

Continuous CV test

Table S3. The results of continuous CV test for three electrodes per each group

Electrodes	Z at 1 kHz (kΩ) Before	Z at 1 kHz (kΩ) After	Z change (%)	CSC (μC/cm^2)					
				Total			Cathodic		
				Before	After	Change (%)	Before	After	Change (%)
Graphene	26.98	25.66	-4.9	148	164	10.8	97	117	20.6
	34.60	33.61	-2.8	99	101	2.0	48	56	16.7
	36.64	36.17	-1.3	198	201	1.5	76	106	39.5
Graphene + 15% Pt NPs	17.19	19.83	15.4	738	675	-8.5	596	548	-8.0
	17.23	21.22	23.1	656	694	5.8	589	635	7.8
	18.03	17.99	-0.3	767	834	8.7	646	703	8.8
Graphene + 30% Pt NPs	12.69	16.23	27.9	928	924	-0.4	731	757	3.5
	10.90	13.33	22.3	797	789	-1.0	678	659	-2.8
	11.27	12.15	7.8	813	829	2.0	669	658	-1.6
Graphene + 40% Pt NPs	7.87	8.62	9.5	879	1004	14.2	727	780	7.3
	7.62	8.53	12.0	952	1112	16.8	755	812	7.5
	9.22	8.80	-4.6	917	1097	19.6	709	827	16.6

EDX result



Element	Weight %	Atomic %
C K	4.01	6.94
O K	44.43	57.73
NaK	3.05	2.76
SiK	41.12	30.43
PtM	4.56	0.49
ClK	2.82	1.65

Figure S2. EDX result (a) Microscopy and SEM image of the electrode after the continuous CV (The zoomed-in optical image shows the dendritic pattern created by Na and Cl residues on the electrode surface), (b) EDX map spectrum and table of the present elements.

Ultrasonic test

The graphene electrodes without NPs showed partial to complete delamination of the layer after only 2 minutes of the ultrasonic test as shown in Figure S3 (a). This is due to the poor adhesion of graphene to the underlying oxide. Samples with NP coatings were able to sustain ultrasonication longer than samples without NPs.

After 5 minutes of ultrasonication, there was visible delamination of the graphene layer on samples with NPs. However, the impedance (at 1 kHz) of the electrode (as shown in Figure S3. (b)) is 13 kΩ which is still much lower than the average impedance of the graphene (34 kΩ), thus implying that there are still Pt NPs on the electrode surface. However, the Pt NP surface density after this duration is unknown. The impedance value is still low (26.25 kΩ) after the 7 minutes of ultrasonication and increases (38.7 kΩ) after 10 minutes. Despite the substantial delamination of the graphene layer, the impedance only increased by about 4 kΩ. This suggests that there may still be some Pt NPs on what is left of the graphene layer. There was also a color change on the graphene after 12 minutes, possibly caused by substantial delamination of the Pt NPs.

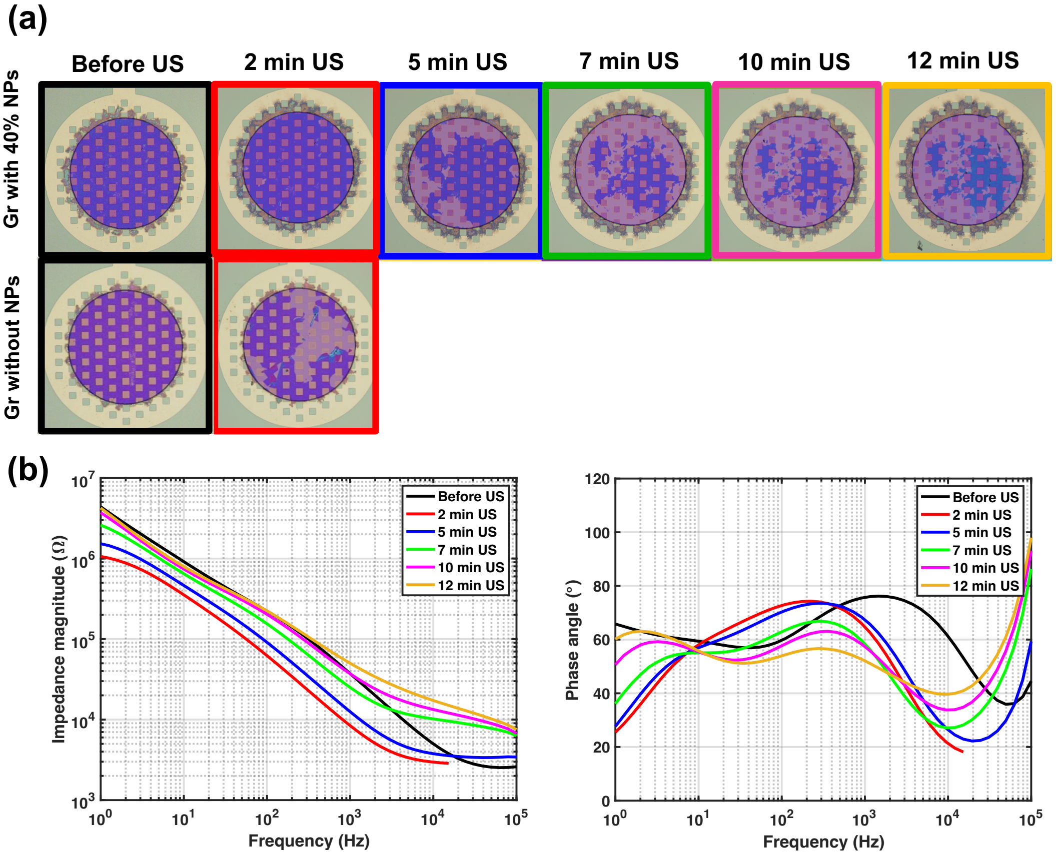


Figure S3. Ultrasonic test (a) optical image of graphene electrodes with and without NPs before and after 12 minutes of ultrasonication, (b) Impedance magnitude and phase plot of graphene electrodes with 40% NPs before and after 12 minutes of ultrasonication.