Supplementary Information: DNA-cisplatin Modified Single-Walled Carbon Nanotubes for the Hydrogen Evolution Reaction

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S1 Experimental Section

Materials and Reagents

Commercial purified SWCNTs were supplied by Nano-C (Batch (PT1112-88WP), Nano-C PT, 33 Southwest Park, Westwood, MA 02090) and were used as received, having been purified of the metal catalyst and residual amorphous carbon using an oxidative acid and/or sequences consisting of acid leaching and oxidation. All chemicals involved were of analytical grade and used without any purification. Sodium perchlorate (≥ 98%), perchloric acid (70%, 99.99% trace metals), salmon milt DNA in the form of its sodium salt, and cisplatin (64.5% min Pt content) were all purchased from Sigma Aldrich. Isopropanol (IPA, reagent grade > 99 %) was purchased from Fisher Scientific. All electrolytes were made up with ultrapure water (resistivity ≥ 18.2 MΩ.cm) (MilliQ, Millipore) and thoroughly degassed with dry nitrogen (oxygen-free, BOC Gases plc) prior to experimentation.

Synthesis and characterisation of DNA-cisPt adducts

DNA-cisPt adducts were synthesised in the same way described in our previous work.[1] In brief this involved dissolving salmon milt DNA in Milli-Q water (resistivity ≥ 18.2 MΩ.cm) followed by sonication to make a stock solution of the desired concentration. Then, cisPt in aqueous form, of a 1 mM, was mixed with the DNA and incubated at 37 °C overnight for 10 hours. Confirmation of the adduct formation was achieved using spectrophotometry and circular dichroism (CD) using a Shimadzu UV-1800 spectrophotometer, Jasco J-810 spectropolarimeter, and a Cary 5000 UV-Vis-NIR Spectrophotometer.[1]

Fabrication of SWCNT-DNA-cisPt material

Initially to disperse the SWCNTs prior to adsorption of the DNA-cisPt adducts, they were sonicated continuously for 90 minutes in a 50% v/v IPA aqueous solution to achieve full dispersion. A 1 mM dispersion of SWCNTs was prepared in a 50% v/v IPA aqueous solution via probe sonication using a 130 Watt ultrasonic processor, VCX 130 (Sonics). A Titanium alloy (Ti-6Al-4V) probe tip was used to break up the SWCNTs. The nanotubes were sonicated for 90 minutes until an adequate dispersion was achieved (as shown in figure S1), equivalent to an energy input of 702 kJ. To prepare the functionalised SWCNTs, a desired volume of the dispersed aqueous solution of the SWCNTs was sonicated with the prepared DNA-cisPt, DNA or cisPt aqueous solutions at the volumes needed to achieve the desired mass loadings and molar ratios. The water bath was kept at a constant temperature of approximately 9-10 °C using ice.

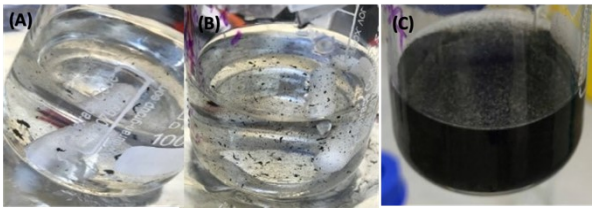


Figure S1. Observable changes in the dispersion of the SWCNTs with increasing time of sonication after (**A**) 0 min; (**B**) 15 min; (**C**) 90 min.

Mass loadings of cisPt and SWCNTs

Using the expression below, we can calculate the platinum mass loading in the samples based on the aliquot volume and the concentration of the prepared samples.

$$C = \frac{n}{V} \; Eq.(1)$$

$$\therefore n = C \times V = \left(1000 \times 10^{-6}\right) molL^{-1} \times \left(25 \times 10^{-6}\right) L = 2.5 \times 10^{-8} \, mol$$

Given the molecular weight of cisPt we can calculate the platinum loading as shown:

$$Mass = n \times M_r \;\; Eq. (2)$$

$$= 2.5 \times 10^{-8} \, mol \times 300.01 \, gmol^{-1} = 7.5 \, \mu g$$

Therefore, for the SWCNT-cisPt material, the mass loading of cisPt in a 25 µL aliquot would be equivalent to 50 % v/v i.e. 12.5 µL is cisPt, which is equivalent to a mass loading of 3.75 μg.

For the prepared 1000 µM stock sample in 50 mL, we have 60 µg of SWCNT in this volume. Hence in an aliquot of 25 µL this equates to 0.3 µg. Hence considering the volume percent, we can estimate the mass loadings of the SWCNTs, as summarised in Table S1.

Table S1. *Mass loading of Platinum and SWCNTs in the SWCNT:DNA-cisPt based catalysts*

Sample Identifier	Description	Molar ratio SWCNT:cisPt	Mass loading of cisPt in catalyst film /µg	Mass loading of SWCNT in catalyst film /µg
4:1 SWCNT:DNA-cisPt	SWCNTs modified with DNA-cisPt complex	4:1	0.75	0.24
2:1 SWCNT:DNA-cisPt	SWCNTs modified with DNA-cisPt complex	2:1	1.25	0.20
1:1 SWCNT:DNA-cisPt	SWCNTs modified with DNA-cisPt complex	1:1	2.50	0.10
0.5:1 SWCNT:DNA-cisPt	SWCNTs modified with DNA-cisPt complex	0.5:1	2.50	0.05
1:1 DNA-cisPt	DNA-cisPt complex only mixed in ratio 1:1 (no SWCNTs)	n/a	3.75	0.00
SWCNT-cisPt	SWCNTs with cisPt	1:1	3.75	0.15

	adsorbed			
cisPt	Bulk (1 mM)	n/a	7.50	0.00

Electrochemical Testing

Electrochemical experiments were conducted in a 3-electrode cell, using a glassy carbon electrode (GC) (d = 3mm, BASi) as the working electrode, a saturated calomel (SCE, BASi) reference electrode and a bright platinum mesh counter electrode. The cell was controlled by an Autolab 128N potentiostat running Nova 2.1 software (Metrohm-Autolab BV, Netherlands). All potentials are reported against the SCE, and all supporting electrolytes were 0.1 M to ensure full support was provided. The GC electrodes were polished on micro-cloth pads with decreasing size alumina slurries (1.0, 0.3, 0.05 μm, Buehler IL), followed by rinsing with ultrapure water and drying under a gentle flow of nitrogen. Once dry, the electrodes were modified by drop casting an aliquot of the prepared SWCNT-DNA-cisPt sample (25 μL) and drying under a lamp. The voltammetry was performed in 1 mM $HClO_4$ and 0.1 M $NaClO_4$ and recorded at a voltage scan rate of 50 mV s^{-1} to observe the HER.

STEM-HAADF

The surface morphology of the material was attained using Scanning Transmission Electron Microscopy (STEM) operated in both Dark field and Bright field imaging using a JEOL2100F instrument. The STEM was operated in Z-contrast mode using a HAADF detector at 200 keV acceleration voltage. All stage alignment was achieved using gold nanoparticles on a Cu carbon TEM grid. The sample was prepared by drop casting 3 μL of the prepared material onto a 300 mesh Cu TEM grid, which was dried under a lamp. STEM-EDX imaging was employed to assess the purity of the carbon nanotubes from metals prior to functionalization.

Analysis of particles was performed using ImageJ software to obtain sizes, based on the TEM images obtained. Single atoms were excluded from the analysis, but all other particles that could be reliably discriminated (due to focus) were included.

X-ray Photoelectron Spectroscopy (XPS)

XPS was used to assess the elemental composition and surface chemical properties of the SWCNT. This was conducted at Harwell XPS (UK) facility using α-Kl as the X-ray source, with a characteristic energy of 1486.68 eV. Analysis was made using CasaXPS software.

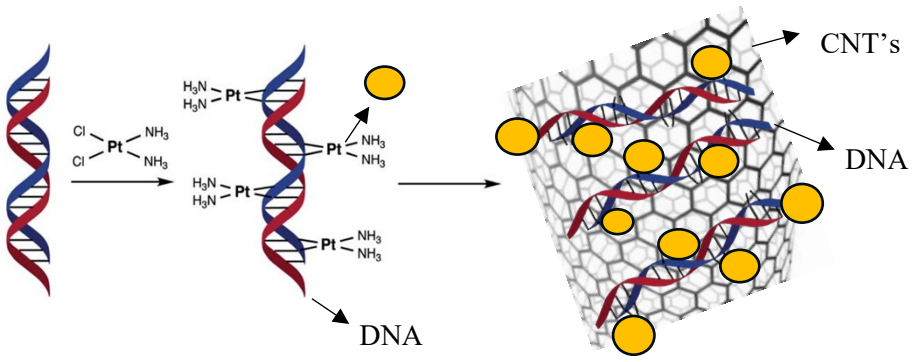


***Figure S3**. Schematic representation of DNA-cisPt adducts used to functionalise Single Walled Carbon Nanotubes (SWCNTs).*

S2: STEM imaging Characterisation

Nanocluster size measurements at different sonication times:

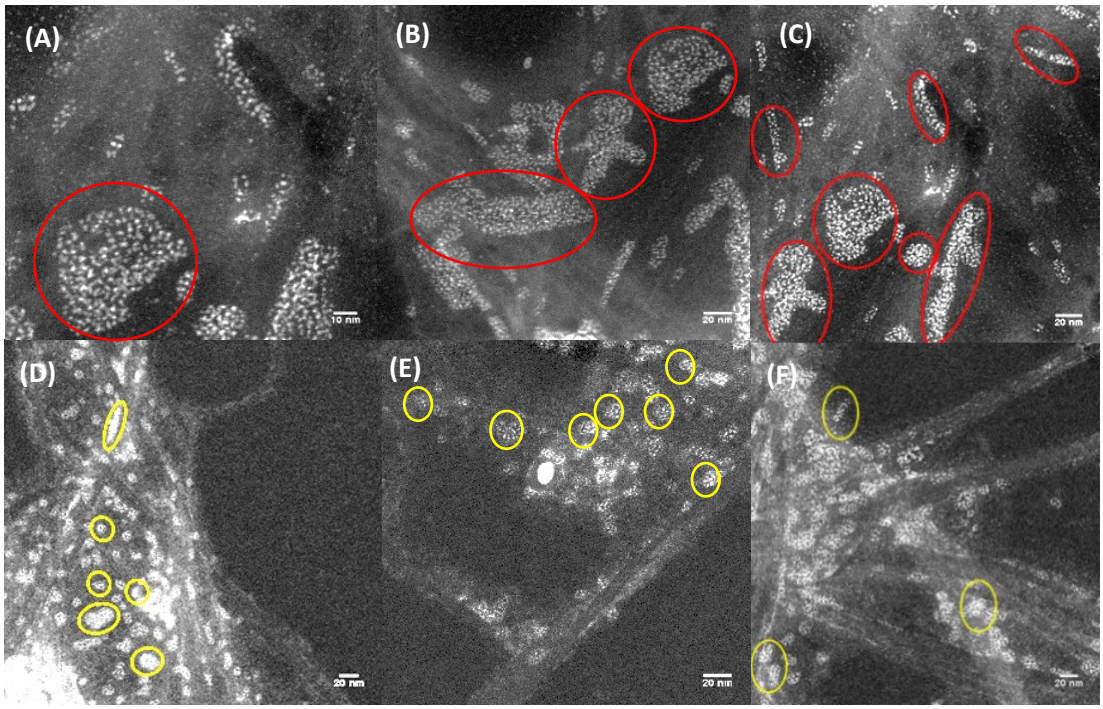


***Figure S4.** 2:1 SWCNT:DNA-cisPt preparation at different sonication times (A-C) 15 minutes (cisPt nanoclusters highlighted in red) (A) × 1000 k (B) ×600 k (C) × 600 k (D-F) 90 minutes (cisPt nanoclusters highlighted in yellow) (D) × 400 k (E) × 600 k (F) × 400 k.*

Table S2. *Data measurements of the nanocluster size at 15 minutes sonication of the 2:1 SWCNT: DNA-cisPt based on STEM Images in Figures S4 (**A**) to (**C**). Particles sized to nearest 0.1 nm to account for error inherent in instrument and image analysis.*

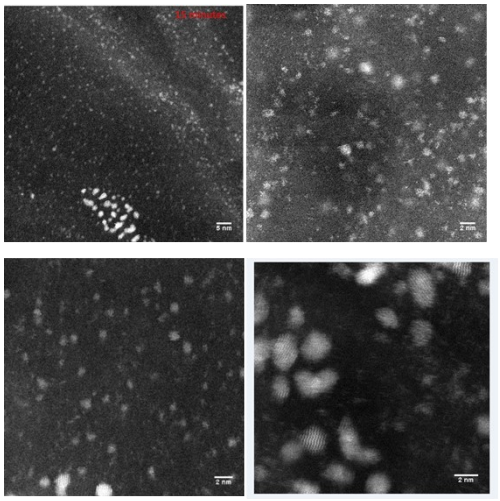
Measurement number	**Particle size / nm**
1	58.1
2	48.6
3	19.2
4	61.1
5	105.2
6	73.5
7	41.3
8	45.4
9	35.1
10	46.0
11	22.1
Average ± Standard deviation error	50.1 ± 24.2 nm

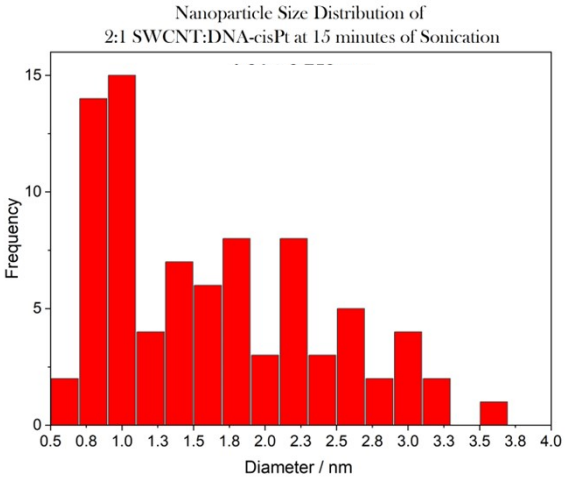
Table S3. *Data measurements of the nanocluster size at 90 minutes sonication of the 2:1 SWCNTs: DNA-cisPt based on STEM Images in Figures S4(D) to (F).*

Measurement number	**Particle size / nm**	**Measurement number**	**Particle size / nm**	**Measurement number**	**Particle size / nm**	**Measurement number**	**Particle size / nm**
1	12.3	12	29.0	23	16.8	34	7.2
2	19.5	13	7.5	24	8.1	35	9.5
3	8.5	14	5.7	25	6.3	36	11.2
4	17.4	15	17.2	26	5.4	37	8.7
5	10.5	16	6.4	27	10.7	38	8.4
6	10.5	17	15.2	28	8.7	39	9.6
7	11.4	18	31.2	29	19.3	40	10.6
8	11.1	19	7.9	30	11.9	41	10.2
9	8.3	20	14.2	31	7.6	42	11.4
10	12.5	21	16.7	32	10.1	43	7.2
11	12.3	22	8.7	33	9.7	44	9.5
Average ± Standard deviation error	12.3 ± 2.7 nm						

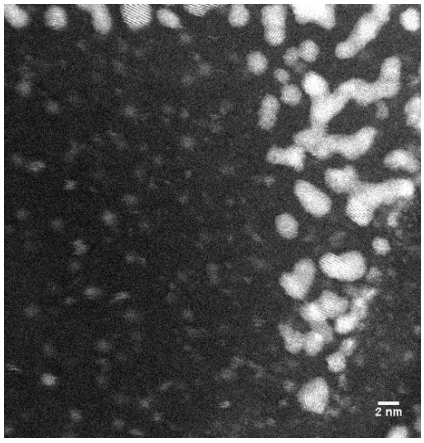
Particle Size Distributions (PSD) of Pt for three-component SWCNT-DNA-cisPt catalysts under various conditions and ratios

(A)





(B)



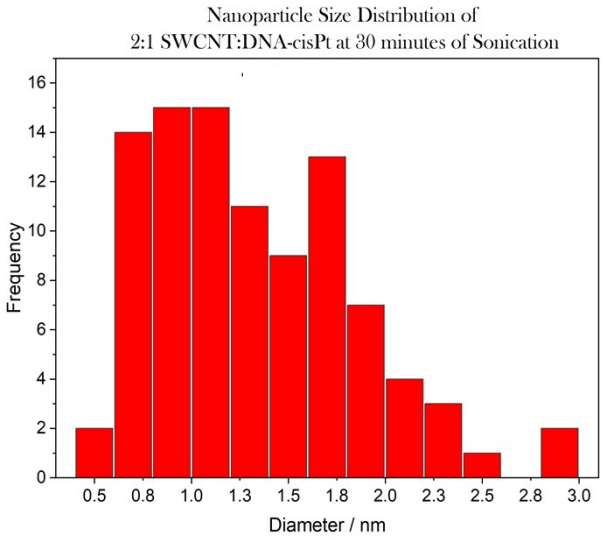
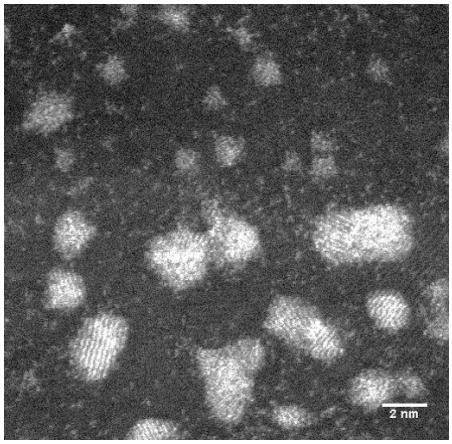
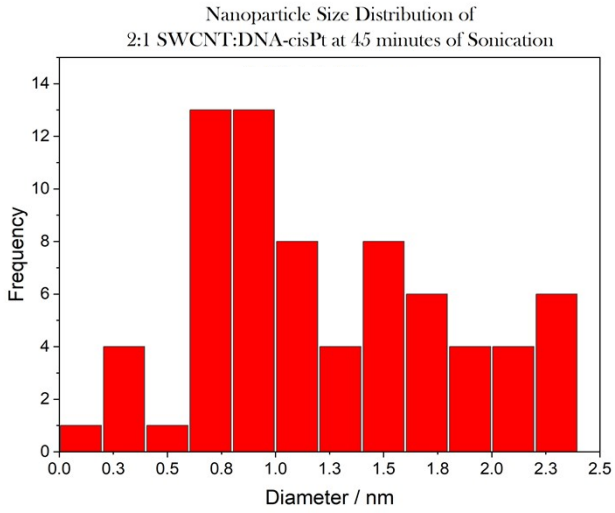


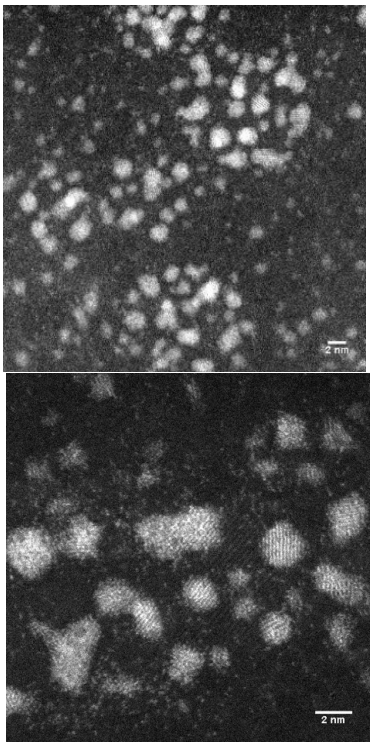
Figure S5. *Particle Size Distributions of Pt nanoclusters from measurements made using the STEM images displayed for the 2:1 SWCNT: DNA-cisPt prepared at (A) 15 mins (average Pt size: 1.64 ± 0.76 nm) (B) 30 mins of sonication mins (average Pt size: 1.32 ± 0.52 nm).*

(C)





(D)



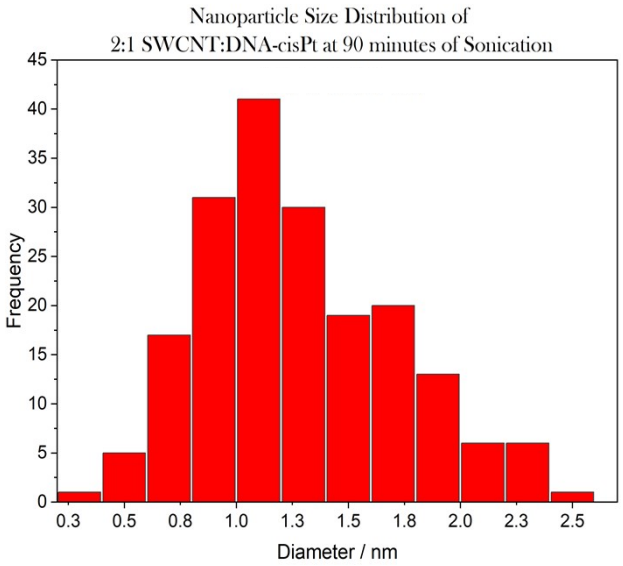


Figure S6. *Particle Size Distributions of Pt nanoclusters from measurements made using the STEM images displayed for the 2:1 SWCNT:DNA-cisPt prepared at* ***(C)*** *45 mins (average Pt size: 1.23 ± 0.58 nm)* ***(D)*** *90 mins of sonication (average Pt size: 1.27 ± 0.43 nm).*

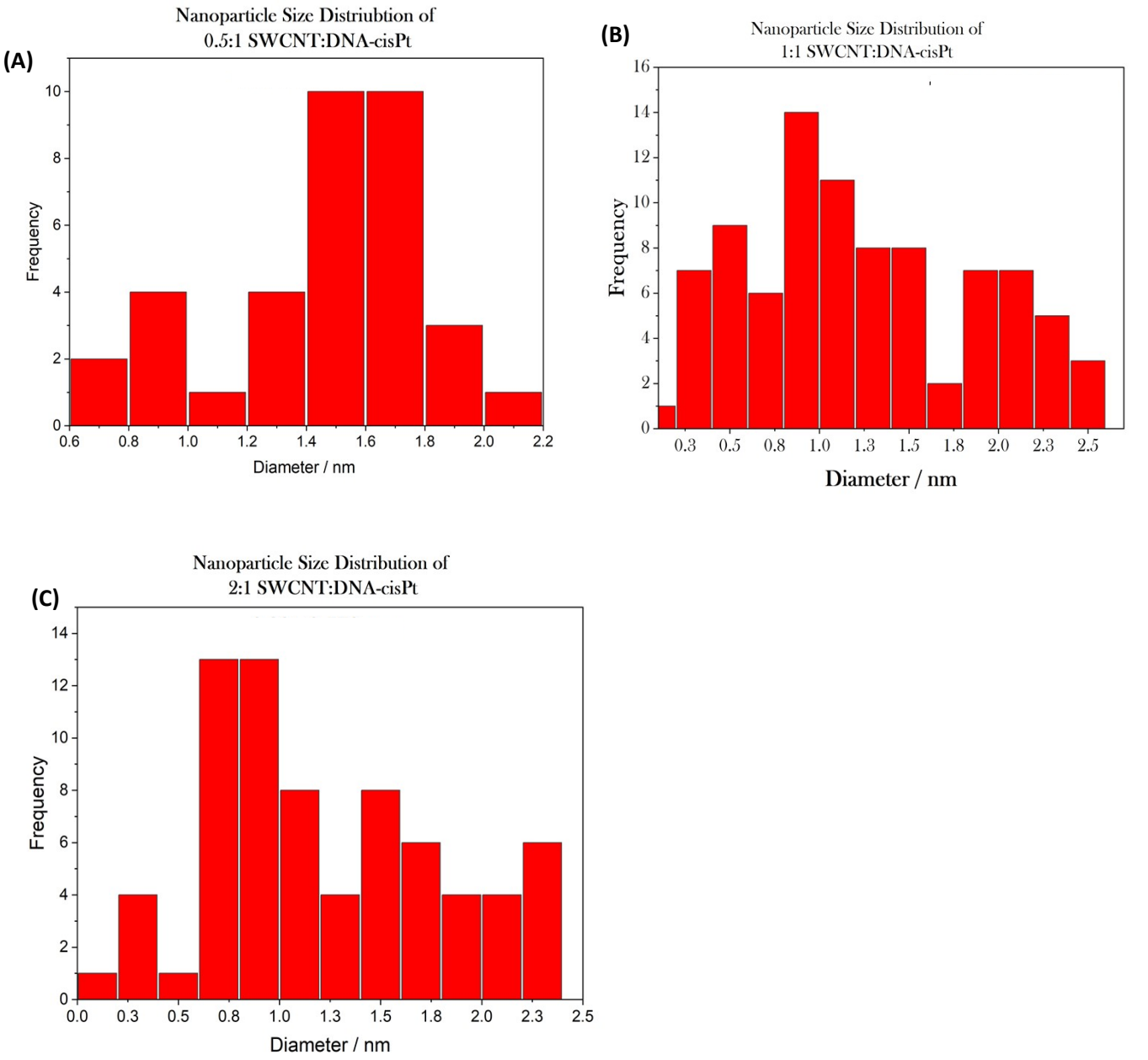
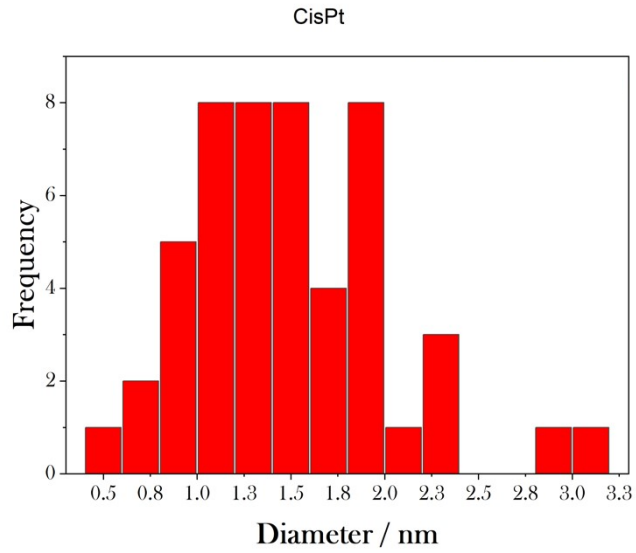
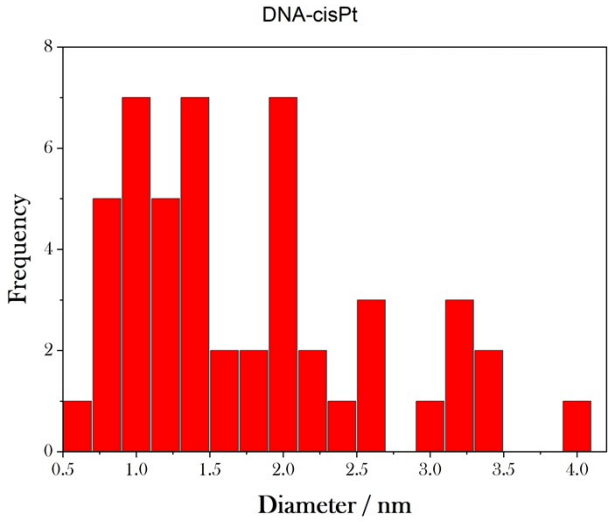
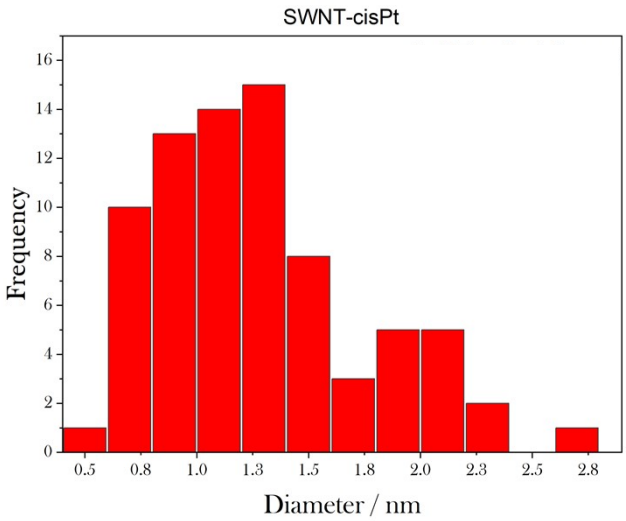


Figure S7. *Particle Size Distributions of Pt nanocluster from the STEM imaging for SWCNT-DNA-cisPt preparations after 45 minutes sonication at different SWCNT:DNA-cisPt ratios of (**A**) 0.5:1 (average Pt size: 1.48 ± 0.34 nm); (**B**) 1 :1 (average Pt size: 1.23 ± 0.65 nm); (**C**) 2:1 (average Pt size: 1.23 ± 0.58 nm.*


CisPt
Frequency
Diameter / nm
0
2
4
6
8
0.5
0.8
1.0
1.3
1.5
1.8
2.0
2.3
2.5
2.8
3.0
3.3


DNA-cisPt
Frequency
Diameter / nm
0
2
4
6
8
0.5
1.0
1.5
2.0
2.5
3.0
3.5
4.0


SWNT-cisPt
Frequency
Diameter / nm
0
2
4
6
8
10
12
14
16
0.5
0.8
1.0
1.3
1.5
1.8
2.0
2.3
2.5
2.8

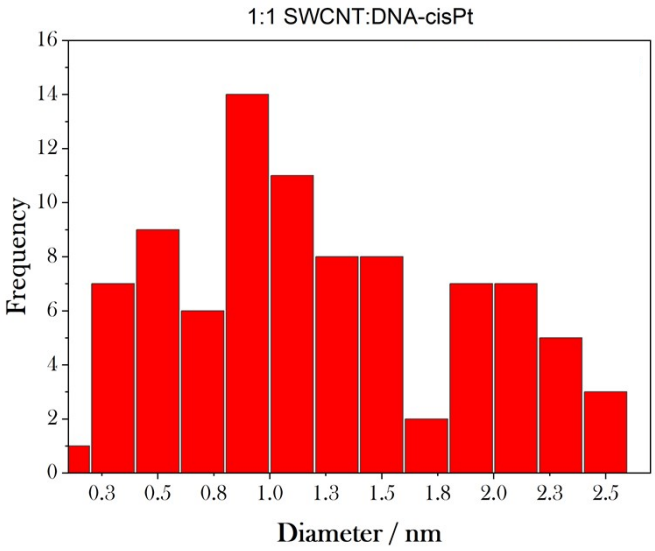

1:1 SWCNT:DNA-cisPt
Frequency
Diameter / nm
0
2
4
6
8
10
12
14
16
0.3
0.5
0.8
1.0
1.3
1.5
1.8
2.0
2.3
2.5

Figure S8. *Size (diameter) distributions of Pt nanoclusters in:* ***(A)*** *cisPt (1 mM) (average Pt size: 1.47± 0.53 nm);* ***(B)*** *DNA-cisPt (average Pt size: 1.77± 0.86 nm) ;* ***(C)*** *SWCNT-cisPt (average Pt size: 1.27± 0.46 nm);* ***(D)*** *1:1 SWCNT:DNA-cisPt (average Pt size: 1.23 ± 0.65 nm), after 45 minutes of sonication.*

STEM Imaging characterisation of DNA vs. DNA-cisPt on SWCNT:

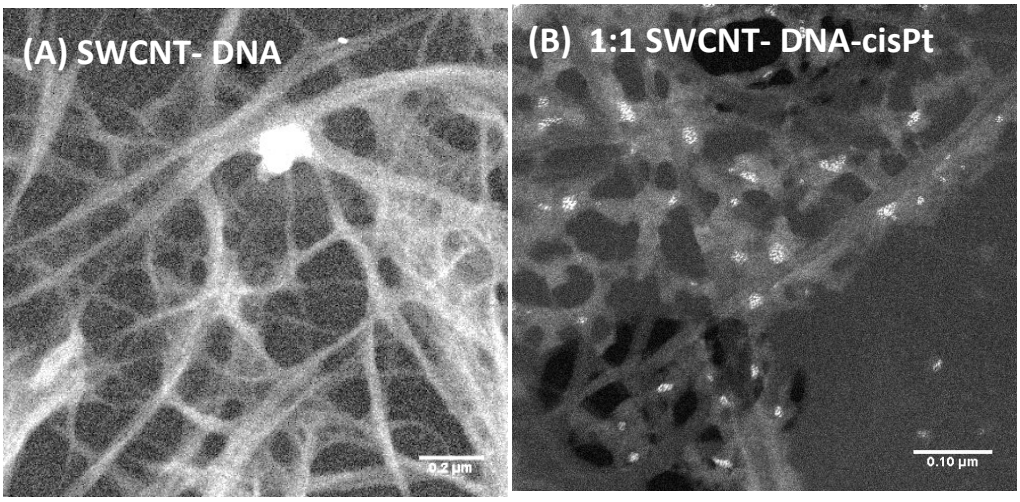


Figure S9.

HAADF STEM images of ***(A)*** *SWCNT-DNA × 100 k magnification* ***(B)*** *1:1 SWCNT -DNA -cisPt × 800 magnification. All films are drop cast from 3 µL solutions onto a 3 mm holey carbon TEM grids.*

STEM EDX characterization:

Elemental mapping of the SWCNT was assessed via STEM-EDX. A region of the prepared TEM grid with SWCNTs drop cast onto the surface undergoes STEM-EDX mapping (figure S10 (A)) to produce the spectrum in figure S10 (B). It is evident that the suspected impurity of iron (Fe) can be ruled out, as shown by the absence of peak in the proposed regions (circled in figure S10 (B)), thus further consolidating the findings of the XPS results. This enables the utilization of the SWCNT for the functionalization reaction with the DNA-cisPt material for the Hydrogen Evolution Reaction (HER) without the need for further purification treatments or concern that the observed electrocatalysis is due to metallic impurities residing on the surface of the SWCNT.

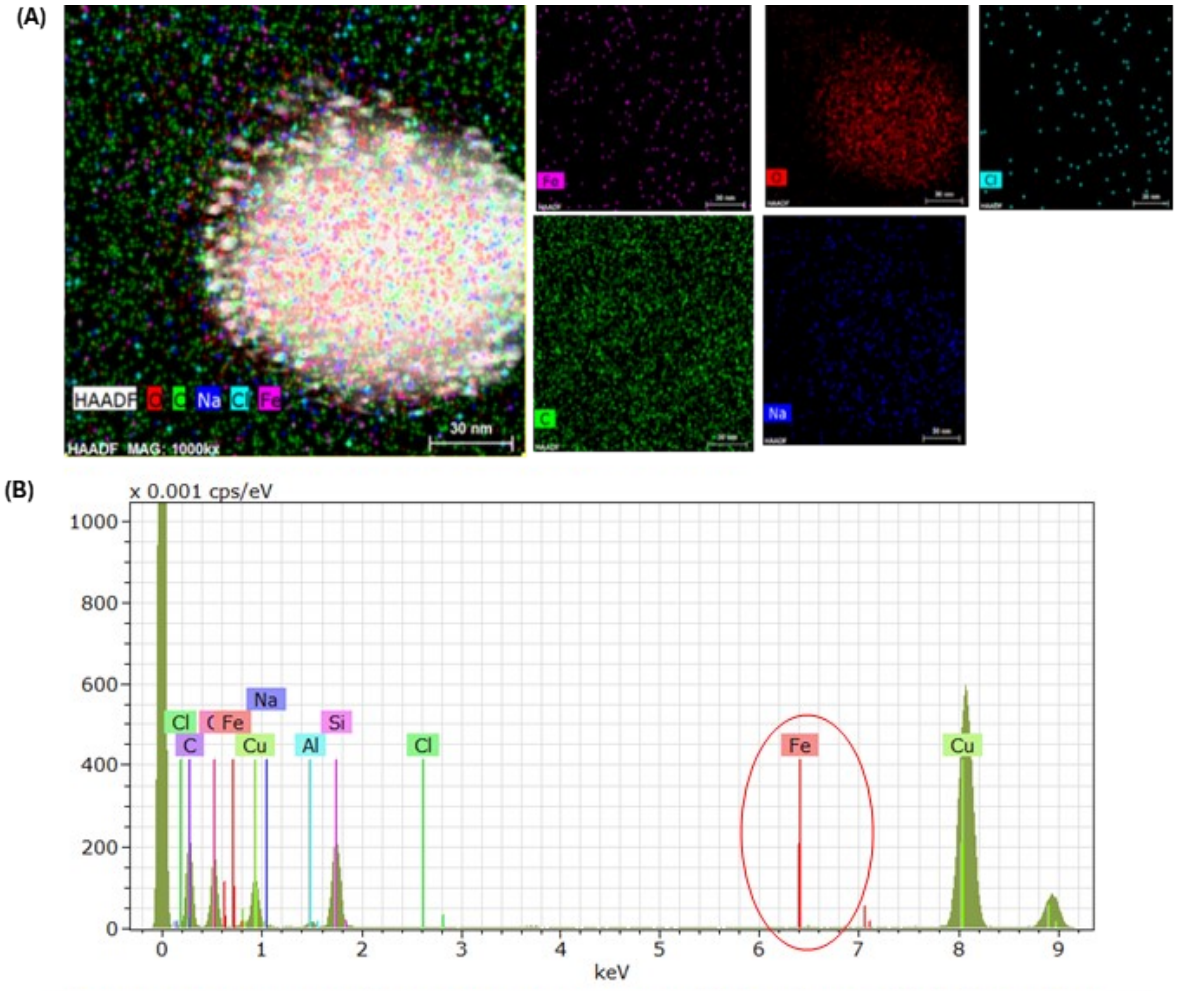


Figure S10*. STEM EDX mapping of* ***(A)*** *1000 µM SWCNTs on a 300-Cu mesh holey carbon TEM* ***(A)*** *distribution of proposed elements/impurities shown* ***(B)*** EDX spectrum , where the red lines mark where the Fe peaks should appear indicating the absence of metal impurities.

S3 Electrochemical Data

The following is Supporting data for Figure 1 and 2 provided in main text.

Table S4 – *Effect of sonication time on electrocatalytic response for the HER and Pt catalyst size for the 2:1 SWCNT:DNA-cisPt catalyst.*

Sonication Time / min	$E_{1/2}$ **/ V vs SCE**	$J_{p,\,max}$**/ mAcm^{-2}**	**Nanocluster size / nm**
15	-0.76 ±0.03	-0.52 ±0.01	1.64 ±0.76
30	-0.63 ±0.04	-0.54 ±0.08	1.32 ±0.52
45	-0.60 ±0.05	-0.54 ±0.07	1.23 ±0.58
90	-0.64 ±0.04	0.51 ±0.05	1.27 ±0.43

Table S5– *Effect of the ratio of SWCNT to DNA-cisPt on the electrocatalytic response for the HER and average Pt catalyst size.*

Ratio of SWCNT: DNA-cisPt	$E_{1/2}$ **/ V vs SCE**	$J_{p,max}$ **/ mAcm^{-2}**	**Nanocluster size / nm**
0.5:1	-0.69 ±0.04	0.53 ±0.06	1.48 ±0.46
1:1	-0.70 ±0.06	0.65 ±0.02	1.23 ±0.65
2:1	-0.67 ±0.01	0.49 ±0.01	1.23 ±0.58
4:1	-0.63 ±0.01	0.50 ±0.01	Not measured

S4: XPS Characterisation

Surface chemical properties of SWCNT: XPS characterization:

The SWCNT samples were prepared and sent to Harwell XPS facilities, (UK) for XPS characterisation of both the unmodified form i.e. solid SWCNT and the dispersed SWCNT form dispersed in 50 % v/v IPA aqueous solution. All the sample preparation was achieved by experienced users at the Harwell XPS team, which involved the drying of the SWCNT in solution onto the sample holder. This was found to contain sodium and other impurities including copper, which is the metal that the sample holder is made from. It was found that the dispersed SWCNTs in 50% v/v IPA aqueous solution was more likely to contain contaminants compared with the solid SWCNT sample.

The XPS results are displayed below:

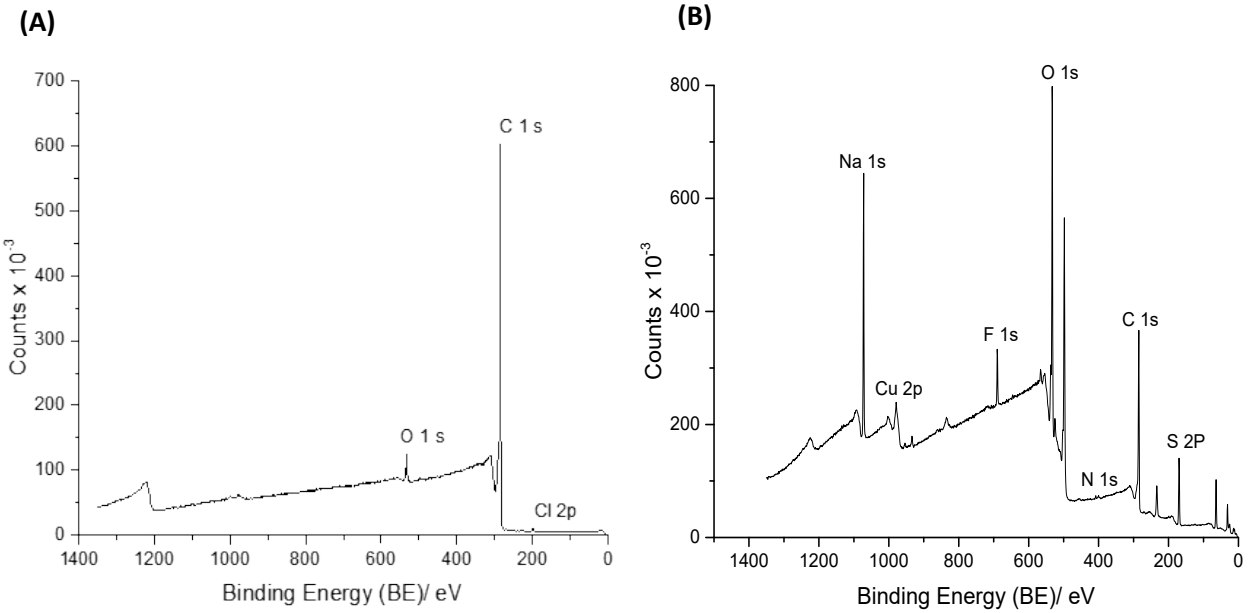


Figure S11. *XPS elemental spectrum of 1000 µm SWCNT (**A**) in as purchased solid form and (**B**) dispersed in 50% v/v IPA aqueous solution.*

***Table S6**. Percentage composition of each element specified based on XPS analysis of SWCNT's in Figure S11.*

Element	Percentage composition / %	
	Aqueous form	**Solid form**
O 1s	31.75	3.02
C 1S	43.42	96.57
Cl 2p	0	0.41
Cu 2p	0.16	
Na 1s	12.37	
S 2p	8.46	
F 1s	3.40	

The two key findings from these XPS results are as follows:

- There are no metallic impurities as initially suspected, such as iron (Fe) which is a commonly employed catalyst during the fabrication process of the SWCNTs.
- Secondly, that dispersion of the SWCNT in a IPA aqueous solution makes the SWCNT more prone to contamination with salt impurities such as sodium, sulphur and fluorine.

References

1. K. Englert, R. Hendi, P. H. Robbs, N. V. Rees, A. P. G. Robinson and J. H. R. Tucker, *Nanoscale Adv.*, 2020, **2**, 4491–4497.