Supporting Information

Controlled fabrication of osmium nanocrystals by electron, laser and microwave irradiation and characterisation by microfocus X-ray absorption spectroscopy

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Materials and methods

Materials. The preparations of the complexes [Os(η^6-*p*-cym)(1,2-dicarba-*closo*-dodecarborane-1,2-dithiolato)] (**1**), [Os(η^6-*p*-cym)(1,2-dicarba-*closo*-dodecarborane-1,2-dithiolato)(triphenylphosphine)] (**2**), and **OsMs** were based on previous reports.[1, 2] The triblock copolymer P123 [poly(ethylene glycol)-*block*-poly(propylene glycol)-*block*-poly(ethylene glycol)] was purchased from Sigma-Aldrich. Anhydrous tetrahydrofuran (Aldrich) was used. 18.2 MΩ·cm purity water was collected from a Purelab® UHQ USF Elga system. Holey carbon grids with 200 gold mesh and lacey carbon grids were purchased from Quantifoil Micro Tools Gmbh and Elektron Technology UK Ltd, respectively.

TEM imaging: TEM data were obtained on a JEOL 2000FX electron microscope at an acceleration voltage of 200 kV. High magnification TEM images were obtained on a JEOL 2100FX electron microscope at an acceleration voltage of 200 kV. TEM samples were prepared on lacey (holey) carbon on 200 mesh gold grids. A drop of sample (5 µL, 1 mg/mL) was deposited on the grid and left to air-dry.

Laser irradiation: A drop of an aqueous solution of **OsMs** (5 µL, 1 mg/mL) was deposited on lacey carbon 400 mesh gold TEM grids (**G2**) as described above. The grids were then irradiated for 5 h using a 1 kHz pulsed laser beam with a pulse duration of 40 femtoseconds (10^{-15} s), generated by a commercially available Ti:sapphire regenerative amplifier (Newport Spectra-Physics Spitfire Pro) seeded by a Ti:sapphire oscillator (Newport Spectra-Physics Tsunami). The wavelength of the laser was centred at 800 nm with a bandwidth of 30 nm (full width half maximum) with an average power of 33 mW to produce Os nanocrystals.

Microwave irradiation: 100 mg of freeze-dried **OsMs** were heated at 190 °C for 8 min at 250 psi in a sealed vessel, using a Biotage Initiator 2.0 microwave synthesizer (400 W). The residue was dissolved in water, and a drop of sample (5 µL, 1 mg/mL) was deposited on a TEM grid and left to air-dry for examination by high-resolution TEM (**G3**).

Microfocus XAFS: All the XAS data were obtained on beamline I18[3]f Diamond Light Source using a Si (111) monochromator. A 5 × 5 micron beam was used for the microXAS data collection in fluorescence mode, while the beam size was increased to 50 × 50 microns to collect the transmission EXAFS data. Fluorescence data were obtained using a 9 element Ortec Ge detector. XAS data were analysed using the Demeter suite of programs Athena and Artemis using multiple scattering paths in the carbon ring for complex **2**.[4] Note that for complex **2** the EXAFS signal is dominated by the S/P shell so the thermal parameters are large for the carbon shells.

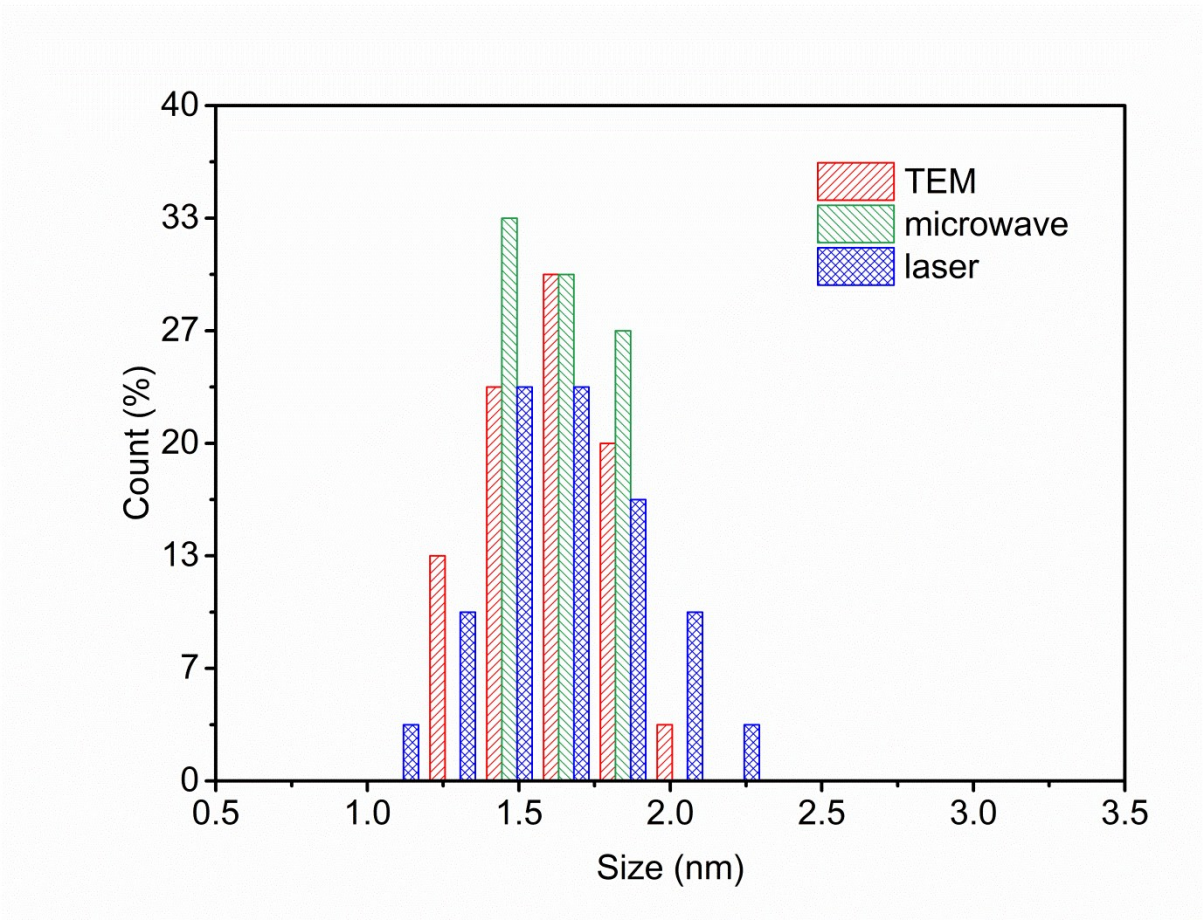

Fig. S1. Size distribution of the nanocrystals produced *via* electron-, microwave-, and laser-irradiation methodologies.

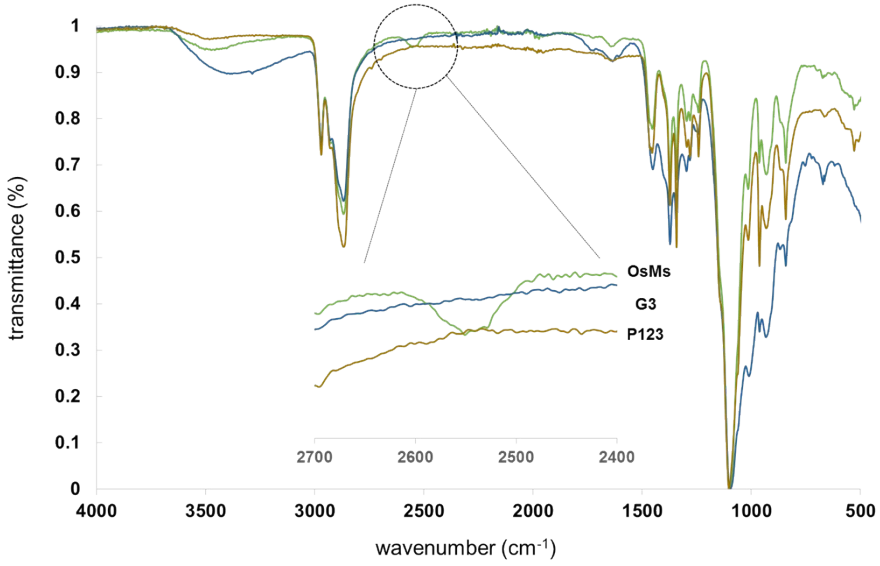

Fig. S2 Infrared spectra of Pluronic P123 (brown), **OsMs** (green) and **OsMs** (**G3**) after microwave irradiation (blue). Inset shows the disappearance of the characteristic carborane B−H stretching vibration band at 2550 cm^{-1} after microwave treatment.

Table S1 XANES analysis of grids. Each region is the average of 4-6 scans.

Sample	Region	White Line Energy / eV	Os Oxidation State
Electron-beam irradiation **G1**	1 (EXAFS)	10877.150	1.30
	2	10877.002	1.00
	3	10877.001	1.00
	4	10877.667	2.34
	5	10877.997	2.99
	6	10877.833	2.67
	Mean	**10877.442**	**1.88**
Laser irradiation **G2**	1 (EXAFS)	10876.900	0.80
	2	10877.563	2.13
	3	10877.166	1.33
	4	10877.274	1.55
	Mean	**10877.226**	**1.45**
Microwave irradiation **G3**	1 (EXAFS)	10876.650	0.30
	2	10877.332	1.66
	3	10876.837	0.67
	4	10877.249	1.50
	5	10876.461	-0.08
	Mean	**10876.906**	**0.81**

Table S2 Fitted EXAFS parameters. S_0^2 is the amplitude reduction factor and E_0 the threshold energy. R_{cryst} is the crystallographic interatomic distance (from the structures indicated in the footnotes) and R_{fitted} the refined interatomic distance. σ^2 is the Debye Waller factor.

Sample	Shell	*N*	***R*cryst / Å**	R_{fitted} / Å	σ^2 / Å^2
18 e complex **2** [Os(η^6-*p*-cym)(1,2-dicarba-*closo*-dodecarborane-1,2-dithiolate)(triphenylphosphine)][1] S_0^2 = 0.83 (fixed) E_0 = 14.0 eV	C	6	2.255	2.24(2)	0.021(7)
	S (P)	3	2.392	2.40(4)	0.004 (3)
	C	2	3.349	3.37(2)	0.016(16)
16 e complex **1** [Os(p-cymene)(1,2-dicarba-closo-dodecarborane-1,2-dithiolate)][2] S_0^2 = 0.81(20) E_0 = -1.543 +/- 3.11 eV	Os	12	2.675	2.660(16)	0.008(2)
	Os	6	3.825	3.76(4)	0.011(4)
Electron Beam irradiated grid 16 hours[3] **G1** S_0^2 = 1.211 +/- 1.04 E_0 = 2.1 +/- 7.4 eV	Os	11	2.675	2.72(8)	0.022(13)
	Os	5.5	3.825	3.90(8)	0.012(10)
	S	2	2.266	2.33(4)	0.006(7)
Laser irradiated grid 5 hours[2] **G2**	Os	12	2.675	2.61(8)	0.010(10)

S_0^2 = 0.83(96) E_0 = -8.507 +/- 13.26 eV	Os	6	3.825	3.64(10)	0.002(10)
Microwave solution grid[2] **G3**	Os	12	2.675	2.61(6)	0.011(7)
S_0^2 = 1.01 +/- 0.82 E_0 = -12.0 +/- 11.5 eV	Os	6	3.825	3.70(10)	0.011(10)

1. Data fitted to crystal structure of ruthenium analogue CSD-QENJUO Herberhold et al.[5]
2. Data fitted to crystal structure of osmium metal published by Swanson and Ugrinic[6]
3. Data fitted to crystal structure of osmium metal published by Swanson and Ugrinic[6] with additional bond sulfur shell

References

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