Electronic Supplementary Material (ESI) for ChemComm.

Supplementary Information

Discovery of face-centred cubic Os nanoparticles

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Chemicals

Osmium(III) chloride hydrate (53.4% Os) was purchased from Aldrich. Sodium acetate (>98.5%), ethylene glycol (>99.0%), sodium tetrahydroborate and poly(N-vinyl-2-pyrrolidone) (K30) were purchased from FUJIFILM Wako Pure Chemicals. Acetylacetone (>99.0%) was purchased from Nacalai Tesque.

Synthesis

For the synthesis of the hcp Os NPs, we used Os chloride hydrate and sodium tetrahydroborate as the precursor and the reducing agent. Os chloride hydrate (35.6 mg) was dissolved in 3.0 mL water. Then, sodium tetrahydroborate (189.2 mg) was mixed into the solution. The solution strongly foamed, and after the reaction completed, the black powder was separated by centrifugation from the solution and washed with water.

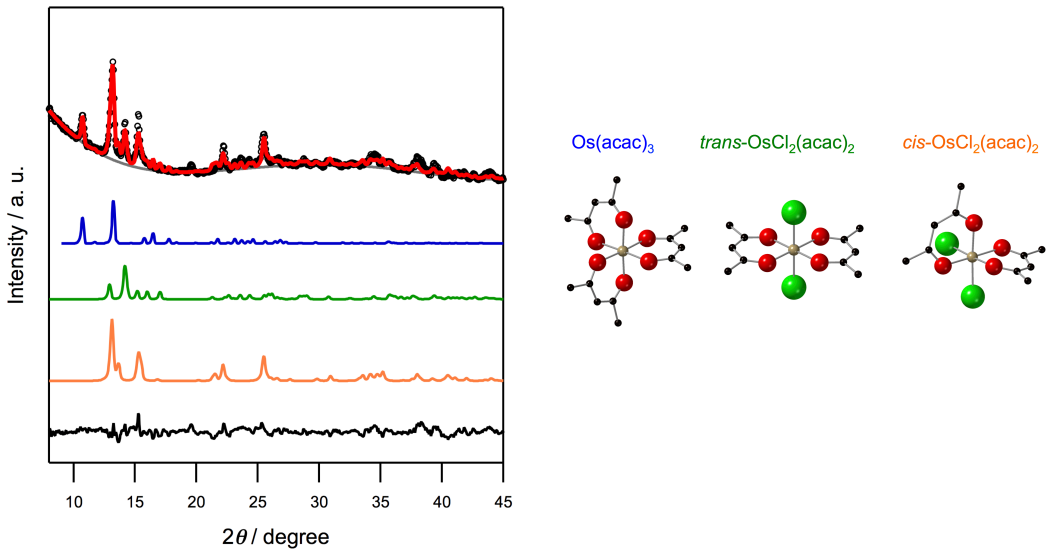

Figure S1. PXRD pattern of the precursor powder and Rietveld refinement. The measurement was performed using Bruker D8 ADVANCE (Cu $K\alpha$). The Rietveld refinement was performed using the TOPAS 5 (Bruker AXS) software: observed pattern (black circle), calculated pattern (red), background (grey), residual (black line), $Os(acac)_3$ (blue), *trans*-$OsCl_2(acac)_2$ (green) and *cis*-$OsCl_2(acac)_2$ (orange). The fitting parameters R_{wp} and S are 4.81% and 2.18, respectively. The proportion of the three compounds is 30.0(3)wt% ($Os(acac)_3$), 25.0(2)wt% (*trans*-$OsCl_2(acac)_2$) and 45.1(2)wt% (*cis*-$OsCl_2(acac)_2$).

	Lattice parameters					
	a (Å)	*b* (Å)	*c* (Å)	α (°)	β (°)	γ (°)
$Os(acac)_3$	13.479(30)	7.673(14)	16.559(15)		98.82(15)	
trans-$OsCl_2(acac)_2$	7.319(10)	7.718(14)	7.893(11)	62.06(15)	86.35(13)	60.533(93)
cis-$OsCl_2(acac)_2$	14.211(16)	8.309(10)	13.696(11)		109.597(95)	

Table S1. Lattice parameters obtained by the Rietveld refinement of $Os(acac)_3$ ($P2_1/c$), *trans*-$OsCl_2(acac)_2$ ($P\bar{1}$) and *cis*-$OsCl_2(acac)_2$ ($C2/c$).

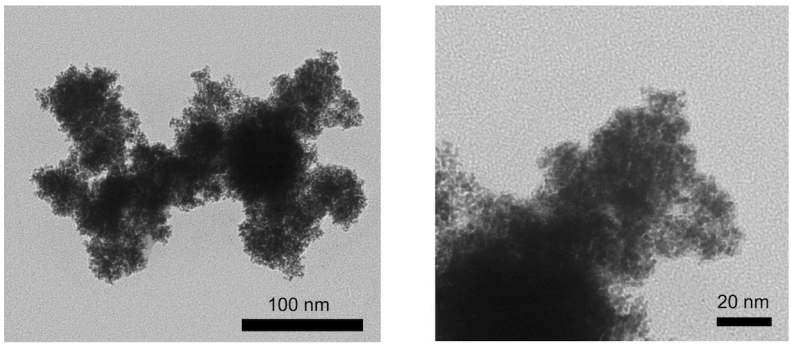

Figure S2. TEM images of the synthesized hcp Os NPs, obtained with Hitachi High-Tech HT7700. The particles were aggregated because of being synthesized without PVP.

Site	x*100	y*100	z*100	Site	x*100	y*100	z*100	Site	x*100	y*100	z*100
1	0	0	0	31	–2τ	–2	0	61	3τ	–1	0
2	0	τ	1	32	1	τ	1+τ	62	0	–3τ	1
3	1	0	τ	33	1+τ	1	τ	63	1	0	–3τ
4	τ	1	0	34	τ	1+τ	1	64	–3τ	1	0
5	0	τ	–1	35	–1	τ	1+τ	65	0	–3τ	–1
6	–1	0	τ	36	1+τ	–1	τ	66	–1	0	–3τ
7	τ	–1	0	37	τ	1+τ	–1	67	–3τ	–1	0
8	0	–τ	1	38	1	–τ	1+τ	68	0	3τ	3
9	1	0	–τ	39	1+τ	1	–τ	69	3	0	3τ
10	–τ	1	0	40	–τ	1+τ	1	70	3τ	3	0
11	0	–τ	–1	41	1	τ	–1–τ	71	0	3τ	–3
12	–1	0	–τ	42	–1–τ	1	τ	72	–3	0	3τ
13	–τ	–1	0	43	τ	–1–τ	1	73	3τ	–3	0
14	0	0	2τ	44	–1	–τ	1+τ	74	0	–3τ	3
15	2τ	0	0	45	1+τ	–1	–τ	75	3	0	–3τ
16	0	2τ	0	46	–τ	1+τ	–1	76	–3τ	3	0
17	0	0	–2τ	47	1	–τ	–1–τ	77	0	–3τ	–3
18	–2τ	0	0	48	–1–τ	1	–τ	78	–3	0	–3τ
19	0	–2τ	0	49	–τ	–1–τ	1	79	–3τ	–3	0
20	0	2τ	2	50	–1	τ	–1–τ	80	2τ+1	2	τ
21	2	0	2τ	51	–1–τ	–1	τ	81	τ	2τ+1	2
22	2τ	2	0	52	τ	–1–τ	–1	82	2	τ	2τ+1
23	0	2τ	–2	53	–1	–τ	–1–τ	83	2τ+1	2	–τ
24	–2	0	2τ	54	–1–τ	–1	–τ	84	–τ	2τ+1	2
25	2τ	–2	0	55	–τ	–1–τ	–1	85	2	–τ	2τ+1
26	0	–2τ	2	56	0	3τ	1	86	2τ+1	–2	τ
27	2	0	–2τ	57	1	0	3τ	87	τ	2τ+1	–2
28	–2τ	2	0	58	3τ	1	0	88	–2	τ	2τ+1
29	0	–2τ	–2	59	0	3τ	–1	89	–2τ–1	2	τ
30	–2	0	–2τ	60	–1	0	3τ	90	τ	–2τ–1	2

Site	x*100	y*100	z*100	Site	x*100	y*100	z*100	Site	x*100	y*100	z*100
91	2	τ	–2τ–1	111	2τ	τ+2	–1	131	2τ+1	0	–τ
92	2τ+1	–2	–τ	112	–1	2τ	τ+2	132	–τ	2τ+1	0
93	–τ	2τ+1	–2	113	–τ–2	1	2τ	133	0	–τ	2τ+1
94	–2	–τ	2τ+1	114	2τ	–τ–2	1	134	–2τ–1	0	τ
95	–2τ–1	2	–τ	115	1	2τ	–τ–2	135	τ	–2τ–1	0
96	–τ	–2τ–1	2	116	τ+2	–1	–2τ	136	0	τ	–2τ–1
97	2	–τ	–2τ–1	117	–2τ	τ+2	–1	137	–2τ–1	0	–τ
98	–2τ–1	–2	τ	118	–1	–2τ	τ+2	138	–τ	–2τ–1	0
99	τ	–2τ–1	–2	119	–τ–2	1	–2τ	139	0	–τ	–2τ–1
100	–2	τ	–2τ–1	120	–2τ	–τ–2	1	140	τ+1	τ+1	τ+1
101	–2τ–1	–2	–τ	121	1	–2τ	–τ–2	141	τ+1	τ+1	–τ–1
102	–τ	–2τ–1	–2	122	–τ–2	–1	2τ	142	–τ–1	τ+1	τ+1
103	–2	–τ	–2τ–1	123	2τ	–τ–2	–1	143	τ+1	–τ–1	τ+1
104	τ+2	1	2τ	124	–1	2τ	–τ–2	144	τ+1	–τ–1	–τ–1
105	2τ	τ+2	1	125	–τ–2	–1	–2τ	145	–τ–1	τ+1	–τ–1
106	1	2τ	τ+2	126	–2τ	–τ–2	–1	146	–τ–1	–τ–1	τ+1
107	τ+2	1	–2τ	127	–1	–2τ	–τ–2	147	–τ–1	–τ–1	–τ–1
108	–2τ	τ+2	1	128	2τ+1	0	τ				
109	1	–2τ	τ+2	129	τ	2τ+1	0				
110	τ+2	–1	2τ	130	0	τ	2τ+1				

Table S2. Atomic sites of Os atoms in the fcc-structured icosahedron model. The atomic sites are obtained referring the report about fcc-structured icosahedron[1]. $\tau = (1 + \sqrt{5})/2$.

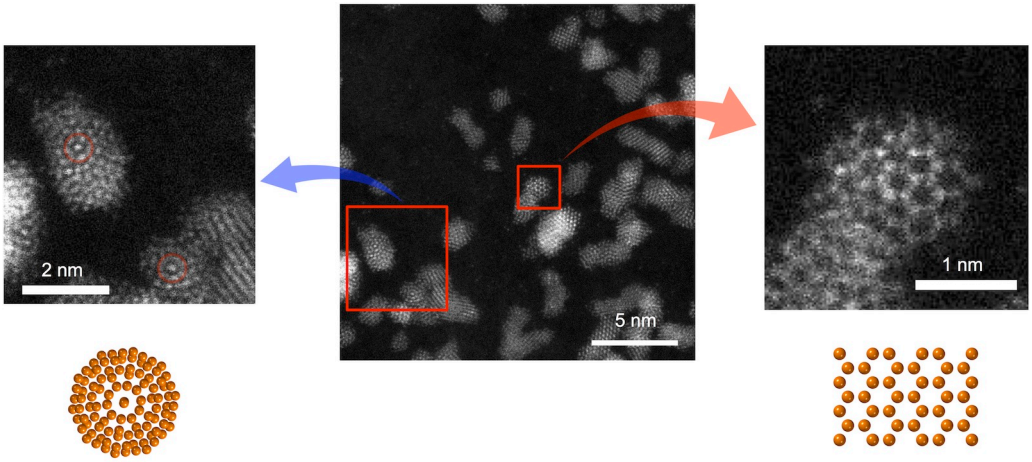

Figure S3. Atomic-resolution HAADF-STEM images of the obtained powder synthesized using the Os acetylacetonate complexes. The magnified image on the left shows fcc-structured icosahedral particles. The magnified image on the right shows an hcp-structured particle. The structural model of hcp Os corresponds to a view along the [001] zone axis.

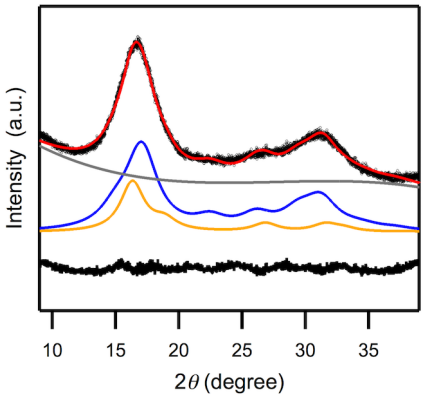

Figure S4. Rietveld refinement of the PXRD pattern of the obtained Os NPs. The patterns are the observed pattern (black circles), fitting pattern (red line), hcp phase (blue), fcc phase (orange) in the fitting pattern, background (gray) and residual (black line). The fitting parameters R_{wp} and S are 3.60% and 4.55, respectively. The proportion is 31(3)wt% (fcc Os) and 69(3)wt% (hcp Os).

	Lattice parameters	
	a (Å)	*c* (Å)
Fcc Os	3.810(9)	
Hcp Os	2.767(7)	4.32(1)

Table S3. Lattice parameters obtained by the Rietveld refinement of the Os NPs

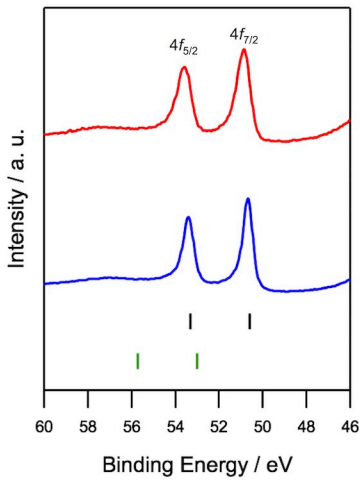

Figure S5. Core-level HAXPES spectra of the obtained powder synthesized using the Os acetylacetonate complexes (red) and the hcp Os NPs synthesized as reference (blue). The black and green bars indicate the Os $4f_{5/2}$ and $4f_{7/2}$ peak positions of Os metal and OsO_2, respectively.[2]

References

1 T. Ogawa, *Z. Physik B*, 1977, **28**, 73

2 B. Folkesson, *Acta. Chem. Scand.*, 1973, **27**, 287.