Discovery of face-centred cubic Os nanoparticles

Journal:	*ChemComm*
Manuscript ID	CC-COM-11-2019-009192
Article Type:	Communication

COMMUNICATION

Discovery of face-centred cubic Os nanoparticles

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

We succeeded in controlling the crystal structure of osmium (Os) nanoparticles (NPs). Although Os adopts only a hexagonal close-packed (hcp) structure in bulk state, a face-centred cubic (fcc) Os was synthesized by a chemical reduction method using an Os acetylacetonate complex as a precursor.

The crystal structure is part of the intrinsic nature of all materials and affects their chemical and physical properties. Most of the transition metals have one of the three basic crystal structures: fcc, hcp or body-centred cubic (bcc). The electronic structure of a transition metal depends on its crystal structure, and the most stable crystal structure is uniquely determined by the total electronic energy of the metal, which is related to the number of electrons of the transition metal.[1] Indeed, in the periodic table of the elements, the hcp–bcc–hcp–fcc structural sequence can be seen as the atomic number increases across the transition metal series. Therefore, selective control of the crystal structure of transition metals has not been freely succeeded.

Nanomaterials have attracted much attention because they show different properties from bulk materials.[2–6] Their pronounced features are tuned by their size, shape and facet, and various methods of controlling their features have been established well.[7–11] Crystal structure control by nanosize effect has been recently reported.[12–14] For instance, Ru NPs with an fcc structure were reported, although Ru has only an hcp structure in the bulk state.[15]

The crystal structure control of Ru was achieved by a proper Ru precursor showing strong interaction between the ligand and Ru, which results in the stabilization of a specific facet of Ru NPs during the reaction. Ru NPs obtained by the reduction of Ru chloride adopt the hcp structure, which is the same as the bulk state.[16] By contrast, when Ru acetylacetonate ($Ru(acac)_3$) is used as the precursor, the synthesized Ru NPs adopts the fcc structure.[15] In situ X-ray absorption fine structure (XAFS) analysis of the formation of fcc Ru NPs suggested that the acetylacetonate ligand coordinated to the surface of fcc Ru NPs during the reaction.[17] The O–O length (2.74–2.93 Å)[18] of the acetylacetonate ligand is close to the nearest-neighbour Ru–Ru bond length (ca. 2.69 Å), and therefore it is considered that the ligand strongly coordinates to the close-packed plane of Ru NPs, which results in the stabilization of the fcc structure by the surface energy contribution because the fcc structure can form unique structures such as icosahedron and decahedron which expose only the close-packed {111} plane.

Here, we have focused on Os for controlling the crystal structure. Like Ru, Os also adopts only the hcp structure and does not adopt the fcc structure in the bulk state even at high pressure and/or temperature.[19,20] Moreover, Os is also considered as an element whose structure in NPs can be controlled by the contribution of the surface energy due to the large surface-to-volume ratio of small NPs, because Ir, the neighbour transition metal of Os, adopts the fcc structure and the difference in total energy between the hcp and fcc structures of Os is assumed to be small.[1] Furthermore, the nearest-neighbour Os–Os bond length (ca. 2.67 Å) is close to the Ru–Ru bond length. Therefore, fcc-structured Os NPs could be synthesized using Os acetylacetonate as a precursor due to the stabilization of the close-packed plane of Os.

In this communications, we report on the crystal structure control of Os NPs. Os NPs were synthesized by using an Os acetylacetonate complex as a precursor in the chemical reduction method. The crystal and electronic structures were investigated by synchrotron powder X-ray diffraction (PXRD) measurements at the SPring-8 beam line BL02B2[21] ($\lambda = 0.6294$

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x

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Å) and atomic-resolution high-angle annular dark-field (HAADF)-scanning transmission electron microscopy (STEM). Hard X-ray photoelectron spectroscopy (HAXPES) measurements were performed at SPring-8 NIMS beam line BL15XU.

For the synthesis of fcc Os NPs, Os acetylacetonate is supposed to be a promising precursor, the same as in the synthesis of fcc Ru NPs. The Os precursor was synthesized referring to the previous reports about synthesis of Os acetylacetonate ($Os(acac)_3$).[22,23] Os(III) chloride hydrate (35.6 mg) was added to 5.0 mL water in an eggplant flask and dissolved well. Next, sodium acetate (205.1 mg) was added to the solution. After the sodium acetate was completely dissolved, 1.0 mL acetylacetone was added to the solution. Sodium acetate was used for pH control in dissolving acetylacetone in water. The solution in an eggplant flask was heated at 100 °C for 6 h in an oil bath, and during the reaction, the colour of the solution changed from greyish black to purplish black. This colour change was consistent with the previous report on the synthesis of $Os(acac)_3$[22] and implied that $Os(acac)_3$ formed in the solution. The obtained solution was filtered and the residue was washed with water. After drying, a purplish black powder was obtained. To investigate the crystal structure of the obtained powder, synchrotron PXRD analysis was performed. Rietveld refinement of the PXRD pattern revealed that the obtained powder contains $Os(acac)_3$,[23] *trans*-$[OsCl_2(acac)_2]$ and *cis*-$[OsCl_2(acac)_2]$[24] (Fig. S1 and Table S1, ESI†). To synthesize fcc Os NPs, poly(N-vinyl-2-pyrrolidone) (PVP) and ethylene glycol were used as the stabilizing and reducing agents, respectively. The obtained Os precursor (59.0 mg) and PVP (20.0 mg) were added to 10.0 mL ethylene glycol in an eggplant flask and the solution was heated at 200 °C for 12 h. After the reaction, the black powder was separated by centrifugation from the obtained solution and washed with water and ethanol. The bright-field (BF)-STEM image confirms the formation of NPs and the mean diameter is 1.2 ± 0.2 nm (Fig. 1). As in the reference, we tried to synthesize hcp Os NPs by using Os(III) chloride hydrate as the precursor. (see SI, Fig. S2, ESI†)

The crystal structure of the obtained NPs was investigated by PXRD analysis. The measurement was performed at ambient condition. In Fig. 2, the NPs synthesized by Os(III) chloride hydrate show the PXRD pattern of the hcp structure to be the same as that of the bulk Os. This pattern shows the typical features of hcp structure, namely that the third peak of 101 reflection is the strongest, at around 17.4°. By contrast, the PXRD pattern of the Os NPs synthesized by using Os acetylacetonate complexes shows very broad peaks due to its small crystalline size. The PXRD pattern is similar to the pattern of fcc Os simulated from the distance of the first nearest-neighbour Os atoms in bulk Os rather than that of hcp Os. This pattern shows the strongest first peak at around 16.6°, where the 111 reflection of the simulated fcc pattern is located. This result indicated the existence of an fcc Os phase. The crystallite size of fcc Os phase was estimated to be 0.6 ± 0.3 nm by Scherrer's equation.

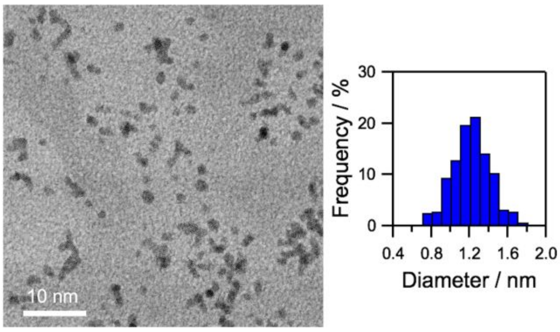

Fig. 1 BF-STEM image of the obtained powder. The histogram was obtained by counting more than 300 particles.

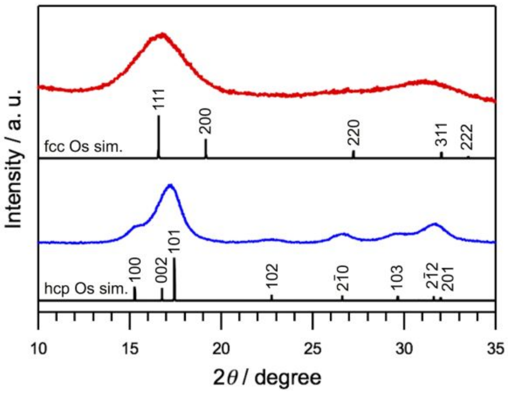

Fig. 2 Synchrotron PXRD patterns of the Os NPs synthesized using the Os acetylacetonate complexes (red) and (blue) Os chloride hydrate, the simulations of fcc (upper black) and hcp Os (lower black).

To confirm the fcc structure of the Os NPs, the atomic arrangement of the obtained Os NPs was directly observed by atomic-resolution HAADF-STEM. Unique multiply twinned structures such as the icosahedron and decahedron are often observed in small fcc-structured NPs such as Au,[25,26] Ag,[27] and even fcc Ru NPs.[15] In particular, icosahedral NPs show the characteristic atomic arrangement of "circle with dot inside", observed by atomic-resolution HAADF-STEM,[28–30] which confirms the formation of an fcc structure. Fig. 3a shows the atomic-resolution HAADF-STEM images of the NPs

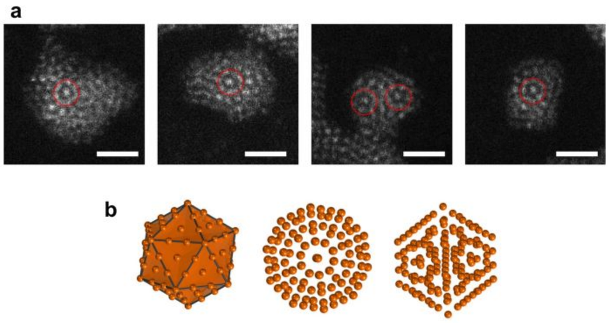

Fig. 3 (a) Atomic-resolution HAADF-STEM images of the Os NPs synthesized using the Os acetylacetonate complexes. The red circles denote examples of "circle with dot inside" indicating icosahedral atomic arrangement. The scale bar is 1 nm. (b) Structural models (Table S2) of fcc-structured icosahedral particle viewed from different directions.

synthesized by using Os acetylacetonate complexes. The red circles indicate the "circle with dot inside" of the icosahedral structure, which cannot be seen in hcp-structured NPs. Given that the previous report indicates that the icosahedral structure shows a weaker 200 reflection than does a non-twinned fcc structure,[31] it is reasonable that the PXRD pattern of the obtained fcc Os NPs does not show the obvious 200 reflection (Fig. 2). The results showed that we succeeded in the first synthesis of fcc Os and confirmed that our hypothesis that the crystal structure of Os NPs can be controlled by Os acetylacetonate. However, in the Os NPs synthesized by Os acetylacetonate complexes, hcp-structured Os NPs were also observed by HAADF-STEM imaging (Fig. S3, ESI†) as an impurity. This might be because the synthesized Os precursor contained not only $Os(acac)_3$ but also *trans*-[$OsCl_2(acac)_2$] and *cis*-[$OsCl_2(acac)_2$]. As the ligand of acetylacetonate promotes the formation of an fcc structure, *trans*-[$OsCl_2(acac)_2$] and *cis*-[$OsCl_2(acac)_2$] containing Cl ligands would not be able to promote the formation of fcc Os NPs. If a pure $Os(acac)_3$ is obtained, pure fcc Os NPs could be synthesized. Indeed, the ratio of $Os(acac)_3$ in the precursor is close to the ratio of fcc phase in the Os NPs obtained from Rietveld refinement (Fig. S4, Table S3, ESI†), which indicates that fcc-structured Os NPs were formed by the reduction of $Os(acac)_3$.

Furthermore, to confirm the formation of fcc Os metal NPs, the valence state of Os was investigated by HAXPES. The core-level Os 4*f* HAXPES of both Os NPs showed peaks located at the same position as for the Os metal, not OsO_2 (Fig. S5, ESI†). This result supports the formation of fcc Os metal NPs.

In summary, we report the first example of fcc Os NPs and proved our hypothesis that crystal structure control of Os NPs can be achieved by using Os acetylacetonate in the chemical reduction method. This result implies that crystal structure control of other transition metals, for example from fcc to hcp or from hcp to bcc, could be realized by using a metal precursor containing an optimum ligand that can stabilize a specific facet. In addition, because fcc Ru NPs show a different catalytic property from hcp Ru NPs,[15] chemical and physical properties of the transition metal NPs could be controlled by controlling the crystal structure. Our report shows a way of crystal structure control and leads to a new development of nanomaterials.

This work has been supported by the ACCEL program, Japan Science and Technology Agency (JST), JPMJAC1501, MEXT KAKENHI Grant-in-Aid for Young Scientists (18K14073) and a Research Fellowship for Young Scientists (17J10244) from Japan Society for the Promotion of Science (JSPS). STEM observations were performed as part of a program conducted by the Advanced Characterization Nanotechnology Platform sponsored by the Minister of Education, Culture, Sports, Science and Technology (MEXT) of the Japanese Government. Synchrotron XRD measurements and HAXPES measurements were carried out at SPring-8 under proposal No. 2017B1257, 2018A1215 and 2019A4907.

Conflicts of interest

There are no conflicts to declare.

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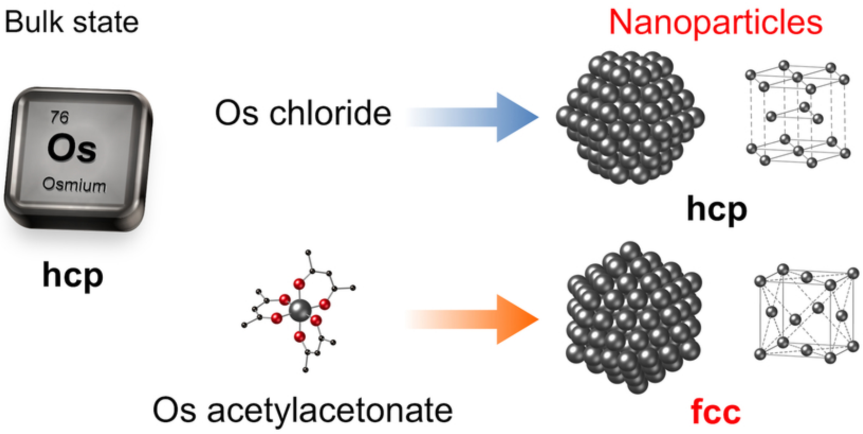
The first example of the crystal structure control of Os is reported. The fcc-structured Os nanoparticles was synthesized using an Os acetylacetonate complex as a precursor although the fcc structure does not exist in the bulk state.



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