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REVIEW

REVISED Osmium and OsO_x nanoparticles: an overview of syntheses and applications

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Abstract

Precious metal nanoparticles are key for a range of applications ranging from catalysis and sensing to medicine. While gold (Au), silver (Ag), platinum (Pt), palladium (Pd) or ruthenium (Ru) nanoparticles have been widely studied, other precious metals are less investigated. Osmium (Os) is one of the least studied of the precious metals. However, Os nanoparticles are interesting materials since they present unique features compared to other precious metals and Os nanomaterials have been reported to be useful for a range of applications, catalysis or sensing for instance. With the increasing availability of advanced characterization techniques, investigating the properties of relatively small Os nanoparticles and clusters has become easier and it can be expected that our knowledge on Os nanomaterials will increase in the coming years. This review aims to give an overview on Os and Os oxide materials syntheses and applications.

Keywords

Osmium, Nanoparticles, Nanomaterials, Catalysis, Synthesis, Clusters, Colloids, Applications

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Any reports and responses or comments on the article can be found at the end of the article.

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REVISED **Amendments from Version 1**

This new version addresses the comments from the reviewers, including in particular regarding the *Theory* section and the *Discussion* section, towards a broader opening on challenges and opportunities in studying Os based nanomaterials.

Any further responses from the reviewers can be found at the end of the article

Plain language summary

Precious metals are rare and expensive materials. However, they present unique properties that make them relevant for many applications, for instance in catalysis and medicine. Numerous studies focus on gold (Au), silver (Ag), platinum (Pt), palladium (Pd), ruthenium (Ru) or rhodium (Rh). Recently, iridium (Ir) is gaining interest for use in developing more sustainable energy conversion. The interest on precious metals extend to less studied materials like osmium (Os). In order to make the most of every atom of these metals, developing nanomaterials like clusters and nanoparticles is a rewarding strategy. With the increasing work and knowledge gained on precious metals in general, it is expected that some of these less studied materials will be opening new opportunities. This review provides an overview of the work performed to date on osmium nanoparticles.

Introduction

Precious metals, such as gold (Au), silver (Ag), platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh) or iridium (Ir), are critical and expensive materials. Nevertheless, they play a key role in catalysis[1,2], water/air treatment[3] and medicine[4]. Molecules comprising one of few atoms or precious metals stabilized by ligands in complexes have been largely investigated for use as catalysts or in medical applications[5]. More recently, nanomaterials made of several hundreds or thousands of metal atoms have been investigated for their unique properties[6] relevant for medicine[4], chemical synthesis and catalysis[7], sensing[8], water/air purification[9], optics[10], electronics[11], building and construction[12], to name only a few examples.

For precious metals, a trend in the literature is to focus on Au, Ag, Pt, Pd, Ru or Rh nanoparticles and nanomaterials. Figure 1 shows the results from a search on the Web of Science (WOS) database (Clarivate Analytics) with different keywords including 'metal' and 'nanoparticles'. These results show the number of references returned for different combination of keywords and metals. A clear trend is that the least studied precious metals are iridium (Ir), rhenium (Re) and osmium (Os) - assuming that the number of references returned for each search gives an indication of the importance of the related research area. This can be explained by the fact that these metals are among the least available on Earth[13]. The focus here is on the least studied material: Os.

Os is the densest metal and has been mainly studied for its mechanical properties[14,15]. However, Os nanomaterials also show promising features for applications in catalysis and medicine[16]. There is, to the best of our knowledge, no review on Os nanoparticles. Os nanoparticles are partially covered in a very recent review witch mainly focuses on Ru and Rh and catalytic applications[2]. In addition to its natural scarcity, the relatively limited amount of work on Os nanomaterials can be inferred to the typically smaller size (<2 nm) for Os nanoparticles compared to other precious metals, for most syntheses

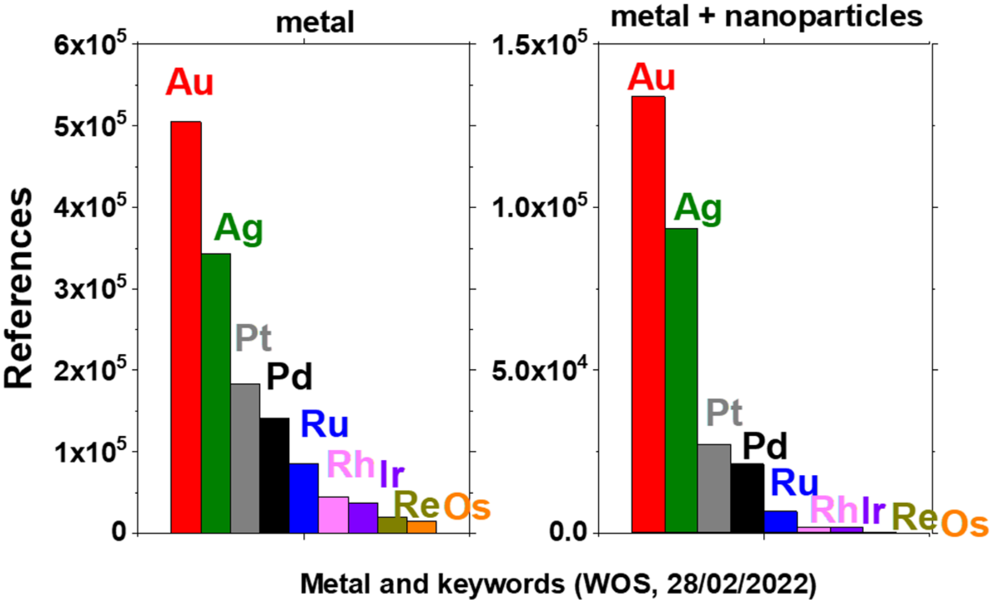

Figure 1. **Number of references returned for searches on the Web of Science database with different keywords, 'metal' or 'metal+nanoparticles', where 'metal' is gold (Au), silver (Ag), platinum (Pt), palladium (Pd), ruthenium (Ru), rhodium (Rh), iridium (Ir), rhenium (Re) or osmium (Os), as indicated.**

reported[17]. This small size makes the nanomaterials challenging to characterize. In addition, the relative limited number of reports on Os can be related to the fact that Os easily get oxidized to OsO_x materials such as OsO_4, a highly toxic compound[18]. Nevertheless, OsO_4 has been commonly used as a staining agent in microscopy[19] and in catalysis[20]. Os complexes and clusters have been used as model systems over many years, for instance in the work of Professor Gates[21]. Based on the knowledge already available on Os complexes, it is expected than the interest and knowledge on Os nanomaterials will grow in the coming years. This review proposes an overview of Os nanoparticles syntheses and applications. Rather than a detailed discussion of selected work, the aim is here to give a broad view of work reported to date on Os nanoparticles, as illustrated in Figure 2.

Discussion/analysis of the recent literature

Formation mechanism

It is expected that understanding the formation mechanism(s) of nanomaterials will be a key to develop more controlled syntheses[22]. This in turn will lead to nanomaterials designed with tuned properties to best match the requirements for a given application. Certainly, materials like Au nanoparticles have been intensively investigated and a relatively clear picture of the nanoparticle formation has been proposed[23,24]. Nevertheless, several questions remain to understand and control how atoms of metal in a complex form larger nanomaterials, e.g. even for the case of well-studied metals like Pt[25]. It can be observed that metals for which the synthesis can easily be followed by simple techniques, such as ultraviolet-visible spectroscopy (UV-vis) for Au or Pt, have been more intensively studied. It is therefore tempting to explain the relatively limited knowledge on Os nanoparticles by the challenging characterization of the related materials. Importantly, the risk of forming the toxic OsO_4[18] is also a bottleneck in the investigation of Os nanoparticles compared to Au or Pt.

A specific feature of Os nanomaterials is to lead to relatively small (<2 nm, see Table 1) nanostructures, regardless of the

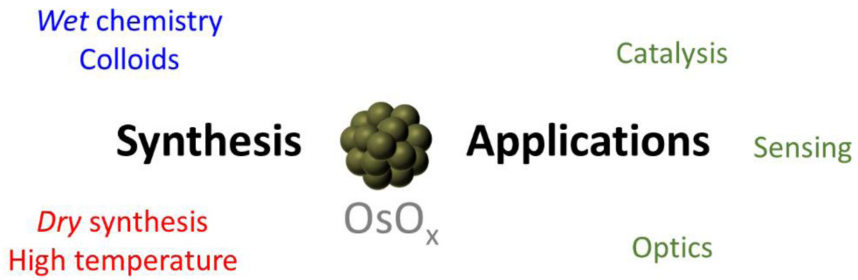

Figure 2. Overview, aim and scope of this review into Osmium oxide (OsO_x).

Table 1. Examples of literature on osmium oxide (OsO_x) nanoparticles synthesis and applications.

Ref	Date	Precursor	Method, solvent, support, additives, conditions	Use	Size / nm
			Dry syntheses		
17	1979	OsO_4	Impregnation	cyclohexene hydrogenation	< 1
26	2007	$[Os_3CO_{10}(NCMe)_2]$	Pyrolysis (acetone) - carbon nanotubes	design of Os nanotubes	< 3
27	2008	Os metal carbonyls	Pyrolysis – SiO_2	-	1-10
28	2012	$Os(C_5H5)_2$	Atomic layer deposition	-	Films and nanoparticles
29	2013	Os(COD) (cyclooctatetraene)	Impregnation (pentane) SiO_2 – H_2 reduction	alkanes hydrogenolysis	1.1
30	2015	Home made Os^{II} complex	Electron beam induced synthesis	-	1.5-50
31	2017	Home made Os^{II} complex	Microwave Laser	-	1-50

Ref	Date	Precursor	Method, solvent, support, additives, conditions	Use	Size / nm
32	2019	Home made Os^{II} complex	Electron beam induced synthesis	temperature effect on nucleation	< 2
Wet chemical syntheses					
17	1979	OsO_4 0.4 mM	Alcohol + water + PVP reflux	cyclohexene hydrogenation	< 1
33	2005	$OsCl_3$ 19 mM	ethylene glycol, NaOH, 160 °C, 3 h	-	0.6-1.8
34	2010	$OsCl_3$ 2 mM	H_2O, HEPES, EPPS, PIPES, MES 180 °C, 1-3 h, autoclave	aerobic oxidation of alcohols to aldehydes	1.6
35	2013	$OsCl_3$	H_2O, AA 95 °C, 1.5 h	SERS	1.0-1.5
36	2014	OsO_4 0.9 mM	H_2O, NaOH CTAB, 2,7-DHN RT, 30 min	catalysis, SERS (nanoparticles or chains)	1-3
37	2014	OsO_4 0.7 mM	DNA, $TBABH_4$ RT, 10 h	cyclohexene hydrogenation SERS	1-3 Shape control
38	2014	OsO_4 0.9 mM	SDS, $NaBH_4$ RT, 30 min	SERS and $KMnO_4$ decomposition (nanoparticles or chains)	1.2-2.5
39	2018	$OsCl_3$	THF, $LiEt_3BH$ RT, 2 h	benzyl alcohol oxidation	1.3
40	2020	K_2OsCl_6 0.2 mM	H_2O, $NaBH_4$, heparin RT, 1.5 h	sensing	1.8
41	2020	$Os(acac)_3$ 12 mM $OsCl_3$ 40 mM	Ethylene glycol, PVP 200 °C, 12 h H_2O, $NaBH_4$, RT	structure control (*hcp* vs. *fcc*)	1-2
42 43	2022	$OsCl_3$ H_2OsCl_6	2.5-100 mM methanol, ethanol, H_2O 85 °C, 6 h – 1 week	-	1-2

AA: ascorbic acid; COD: 1,5-cyclooctadiene; CTAB: cetyltrimethylammonium bromide; EPPS : 3-[4-(2-hydroxyethyl)-1-piperazinyl] propanesulfonic acid; 2,7-DHN: 2,7-dihydroxynaphthalene; HEPES: (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid; MES: 2-ethanesulfonic acid; PIPES: piperazine-N,N′-bis(2-ethanesulfonic acid); PVP: polyvinylpyrrolidone; RT: room temperature; SERS: surface-enhanced raman spectroscopy; SDS: sodium dodecyl sulfate; $TBABH_4$: tetrabutylammonium borohydride; *fcc*: face-centered cubic; *hcp*: hexagonal close packed.

synthesis approach used. For this size range, most characterization techniques, until recently, are not easily implemented to evaluate size, shape and structure or to follow the formation mechanism of Os nanomaterials. Recently, using a combination of complementary *in situ* X-ray diffraction (XRD), quick X-ray absorption fine-structure (QXAFS) and X-ray photoelectron spectroscopy (XPS) performed at synchrotron facilities, the formation at high temperature of PdOs nanoparticles from $[Pd(NH_3)_4][OsCl_6]$ was studied[44]. Such advanced studies are much needed to better understand the formation of nanomaterials but remain scarce for Os and Os based materials. Another example is the use of X-ray total scattering with pair distribution function (PDF) analysis, also requiring access to synchrotron facilities, where Os_xCl_y intermediates structures were suggested for the formation of Os nanoparticles in a colloidal approach[42]. Despite a relatively poor understanding on how Os nanomaterials form, and few reports focusing on the formation mechanism of Os nanoparticles, a range of successful syntheses have been reported and are illustrated in Table 1.

Dry syntheses

As opposed to wet chemical syntheses detailed below, where the formation of Os nanoparticles proceeds in the liquid phase, a range of high temperature dry syntheses are reported for Os nanoparticles. Typically a support material is needed to stabilize the nanoparticles[2]. An overview of different syntheses is proposed and an example of synthesis is the thermal decomposition of Os precursors[45]. Pyrolysis leads to different nanoparticle size depending on the ligand structures of the precursors[27] and needs to be performed at relatively high temperature, e.g. 300 °C, when the precursor is an Os carbonyl complex[26]. Hydrogen (H_2) reduction is also an option[29]. Magnetron sputtering has been reported for Os films[46]. Alternative methods include wet incipient impregnation[47], freeze drying[48] or atomic layer deposition (ALD) of Os films and particles[28]. However, in this last approach and in this specific study, where osmocene and molecular oxygen were used as precursors, the challenge was the formation of highly toxic OsO_4 at high temperature.

Wet chemical syntheses

Wet chemical or colloidal syntheses are very popular synthetic approaches to obtain a range of nanomaterials directly relevant for multiple applications[1,7,49]. The formation of nanoparticles proceeds in a solvent via the reduction of a metal complex in an oxidized state in the presence of a reducing agent[50], followed by the growth of the nanoparticles[51]. In most cases, the syntheses do not require a support material. This is an advantage to truly investigate support and loading-related effects in catalysis since the nanoparticle formation and control over the nanoparticle size and other properties is independent of the presence of a support[52]. Typically, the syntheses are performed in presence of a range of additives like surfactants to stabilize the nanoparticles.

Os nanoparticles can be obtained from a variety of solvents and reducing agents summarized in Table 1. Surfactants typically added for the synthesis are for example heparin[40], (4-(2-hydroxyethyl)-1-piperazineethanesulfonic acid) (HEPES)[34], 3-[4-(2-hydroxyethyl)-1-piperazinyl] propanesulfonic acid (EPPS)[34], piperazine-N,N′-bis(2-ethanesulfonic acid) (PIPES)[34], 2-ethanesulfonic acid (MES)[34], polyvinylpyrrolidone (PVP)[17], sodium dodecyl sulfate (SDS)[38], DNA[37,53], sodium citrate[54] and various precursors are suitable to obtain Os nanoparticles. $OsCl_3$ remains a common precursor. $OsCl_3$ can be reduced at room temperature (RT) using a strong reducing agent like $LiEt_3BH$ (superhydride) in tetrahydrofuran (THF)[39]. The nanoparticles are *circa* 1.3±0.2 nm. $NaBH_4$ is also a suitable reducing agents for RT synthesis[38]. In a range of other syntheses, temperature between 80 to 200 °C are typically used depending on the solvent selected, see Table 1. In methanol-water in presence of PVP, sub-nanometer nanoparticles are obtained[17]. Ionic liquids are also suitable to obtain nanoparticles for instance from the metal carbonyl precursor $Os_3(CO)_{12}$[55,56]. The reaction of OsO_4 in aqueous solution of cetyltrimethylammonium bromide (CTAB), 2,7-dihydroxynaphthalene (2,7-DHN) and NaOH, leads to nanoparticles *circa* 1-3 nm[36]. Adjusting the concentration of CTAB, different morphologies made of individual nanoparticles, chain-like or aggregated clusters were obtained. Chains of Os nanoclusters are also obtained using ascorbic acid (AA) as a reducing and capping agent in an aqueous medium to lead to nanoparticles in the size range 1-1.5 nm with properties suitable for surface-enhanced raman spectroscopy (SERS)[35].

Os nanoparticles are typically small (<2 nm) across different syntheses[34]. This therefore questions the actual need to stabilize the small nanoparticles. Developing surfactant-free colloidal syntheses, although it is challenging, is possible[57]. Surfactant-free nanoparticles with a more accessible surface to reactants are directly relevant for catalysis. Surfactant-free nanoparticles are also more simply modified, for instance with dedicated ligands and molecules towards bio-medical applications. Examples of surfactant-free nanoparticles include the polyol synthesis[33], typically performed in alkaline ethylene glycol, or recently reported mono-alcohol synthesis[1], performed in alkaline methanol or ethanol. In the latter case, it was actually shown that high precursor concentrations up to 100 mM[43] and even without the need for a base[42], leads to the formation of small size <3 nm Os nanoparticles, see Figure 3. Such small size nanoparticles were obtained across a large parametric study investigating the time of synthesis from hours to weeks, nature and concentration of precursors, solvent composition and reducing agent (methanol or ethanol) as well as base concentration.

A recent work showed that face-centered cubic *(fcc)* nanoparticles instead of the expected hexagonal close packed *(hcp)* structure could be obtained by careful choice of the precursor, reducing agent and solvent, see illustration in Figure 4. - Iridium is the neighbor transition metal of Os and adopts the *fcc* structure. The difference in total energy between the *hcp* and *fcc* structures of Os is expected to be small and so it should be possible to obtain *fcc* Os nanoparticles. In presence of ethylene glycol and PVP using Os acetylacetonate ($Os(acac)_3$), *fcc* nanoparticles were obtained whereas *hcp* nanoparticles were obtained with $OsCl_3$ in water using $NaBH_4$ as reducing agent[41]. The change in structure is attributed to the role of the acac ligand that can stabilize the nearest-neighbor Os–Os bond length (ca. 2.67 Å) in a close-packed plane of Os, that is close to the O–O length (2.74–2.93 Å) of the acac ligand. This leads to nanoparticles with a different crystal structure. The question of whether or not this would happen is the synthesis was performed under exactly the same conditions (same precursor concentration, reducing agents and solvents) but only changing the precursor remains open. Size selected nanoparticles were obtained in a two-phase (water-toluene) approach from OsO_4 and tetrabutylammonium borohydride ($TBABH_4$): 1±0.2 nm, 10–30 nm, 22±2 nm and 31±3 nm nanoparticles were synthesized by changing the concentration ratio of the metal precursor and the amount of reductant[37].

Os complexes and clusters

Compared with Os nanoparticles, Os complexes have been more studied to date[20,58–60]. For instance, Os metal carbonyl complexes have been widely investigated[61]. The group of Professor Gates intensively studied Os_n clusters[62,63]. In particular Os carbonyls clusters were widely investigated on various support like gold[64], MoS_2[61], zeolite[65], MgO[62,63,66,67] with a focus on conversion from complexes to clusters. Carbonyls clusters were investigated by ^{129}Xe nuclear magnetic resonance (NMR), where $[HOs_3(CO)_{11}]^-$ or $[H_3Os_4(CO)_{12}]^-$ were found to formed in zeolites[65] and $[Os_3(CO)_{12}]$ on MgO[66].

Barry *et al.* used Os atoms and complexes as their model system for various studies, e.g. to build up 3D nanocrystals to observe, study and quantify crystal growth at the atomic

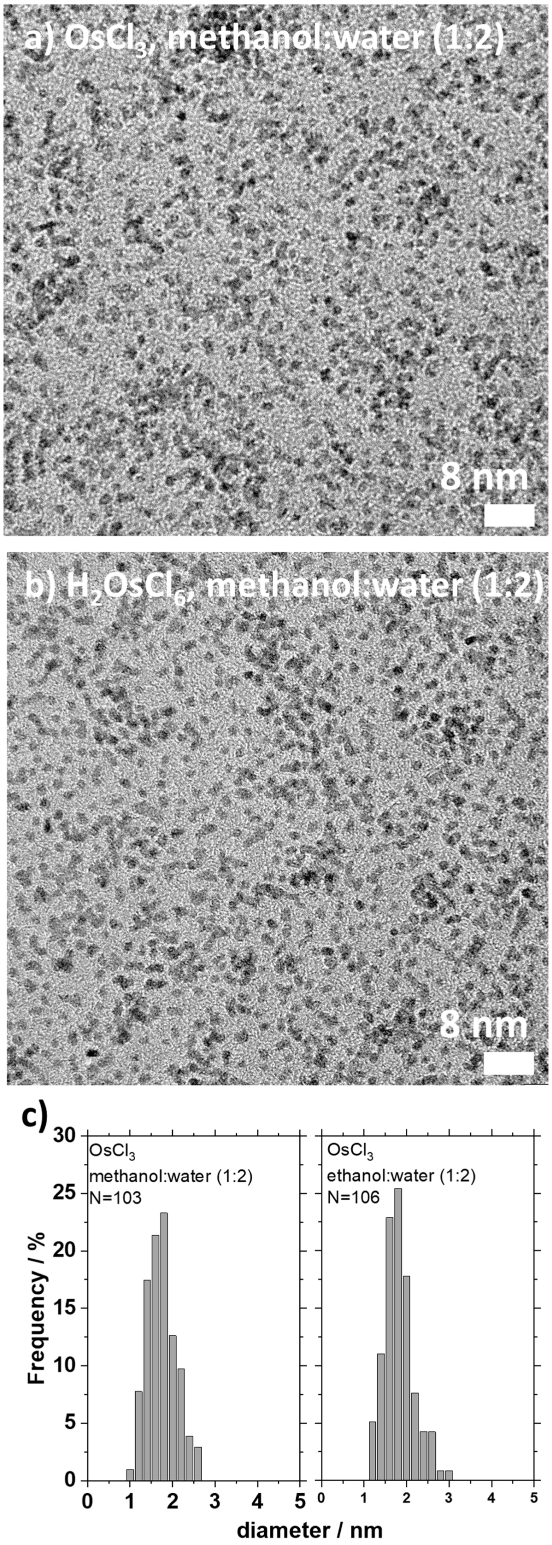

Figure 3. Example of small size Osmium (Os) nanoparticles. (**a**–**b**) transmission electron microscope (TEM) micrographs of Os nanoparticles obtained using water (66 volume %) and methanol (33 volume %) and 100 mM of (**a**) $OsCl_3$ and (**b**) H_2OsCl_6 as precursors after a one-week reaction at 85 °C. The size analysis (**c**) suggests that the nanoparticles are (**a**) 1.6±0.4 nm and (b) 1.7±0.3 nm. Reproduced from 42 with permission from the Beilstein-Institut.

scale controlled in real time[68,69], see the illustration in Figure 5. The experiments were conducted using the electron beam of a transmission electron microscope (TEM) and a micelle-stabilized complex of [Os(*p*-cymene)(1,2-dicarba-*closo*-dodecarborane-1,2-dithiolate)][30]. The same precursor under microwave irradiation leads to supported Os nanoparticles *circa* 1 nm in diameter[31]. Os was used to show the temperature dependent nucleation and growth kinetics of precious metal nanocrystals supported on silicon nitride by aberration corrected TEM[32]. Barry *et al.* for that purpose used homemade Os complexes in that study. The growth rate was found to be dependent on the temperature (*circa* 2.5 times faster at 100 °C than at 20 °C). No effect of the temperature on the crystal structure of the nanocrystals was observed, ''although the sizes of the crystals (<2 nm) and the very small number of atoms per crystal render clear elucidation of the structures extremely difficult''[32]. The challenging characterization of Os nanoparticles by routine equipment indeed remains a bottleneck.

Applications

Os nanomaterials found applications in a wide range of fields and a broad overview is proposed here.

Chemical synthesis. Recent reports suggest that Os nanomaterials might have specific properties for hydrogenation reactions compared to other precious metals[70]. Os based materials have been used as catalysts for dihydroxylation[71], cyclohexene hydrogenation[17,37], citral hydrogenation[72]. Other reactions include oxidation of benzyl alcohol with relatively low yield compared to Ir[39] or reduction of 4-nitro aniline[36]. Using HEPES protected nanoparticles, the conversion of *p*-methylbenzylalcohol[34], *p*-methoxybenzylalcohol[34], *p*-bromobenzylalcohol[34], 3-phenyl-2-propanol[34], 3-phenyl-2-propenol (cinnamylalkohol)[34], 1-phenylethanol[34], lead in all cases to the aldehyde or ketones in relatively high yield. On silica doped with zirconium, Os nanoparticles show reactivity for hydrogenation and hydrogenolysis/hydrocracking of tetralin from aqueous $K_2[OsCl_6]$[47]. A high Os content displays weak hydrogenation activity but very good hydrogenolysis/hydrocracking activity. Os nanomaterials are also suitable for the synthesis of various 1,2-cis-diols[73], 1,2/3-triols synthesis from the allylic hydroperoxides[74], *syn*-dihydroxylation of alkenes[75], reduction of *p*-nitroaniline into *p*-phenyldiamine[76], oxidations reaction[39], CO oxidation[77], ammonia synthesis[78] or Fischer–Tropsch synthesis[79]. Under aerobic condition, oxidation of activated, unactivated and heteroatom containing alcohols to carbonyl compounds lead to high activity and selectivity even under mild conditions[80].

6.2.5.2. Electrochemistry. OsO_x materials have been shown to be suitable for a range of electrochemical reactions including hydrogen evolution reaction (HER)[81], oxygen reduction reaction (ORR)[82] or as direct borohydride polymer electrolyte membrane fuel cell anodes[83]. Freeze drying was used to obtain Os/Si nanowires and the corresponding nanoparticles by etching the Si nanowires[48]. In this comparative study with Rh, Pt, Pd, Re, Ru, Au or Ag nanocomposites, Os was found to give the higher activity for the HER, a small onset potential of -25 mV and long term stability[48]. Using magnetron sputtered Os it was found that the high activity of OsO_x for the HER in acidic

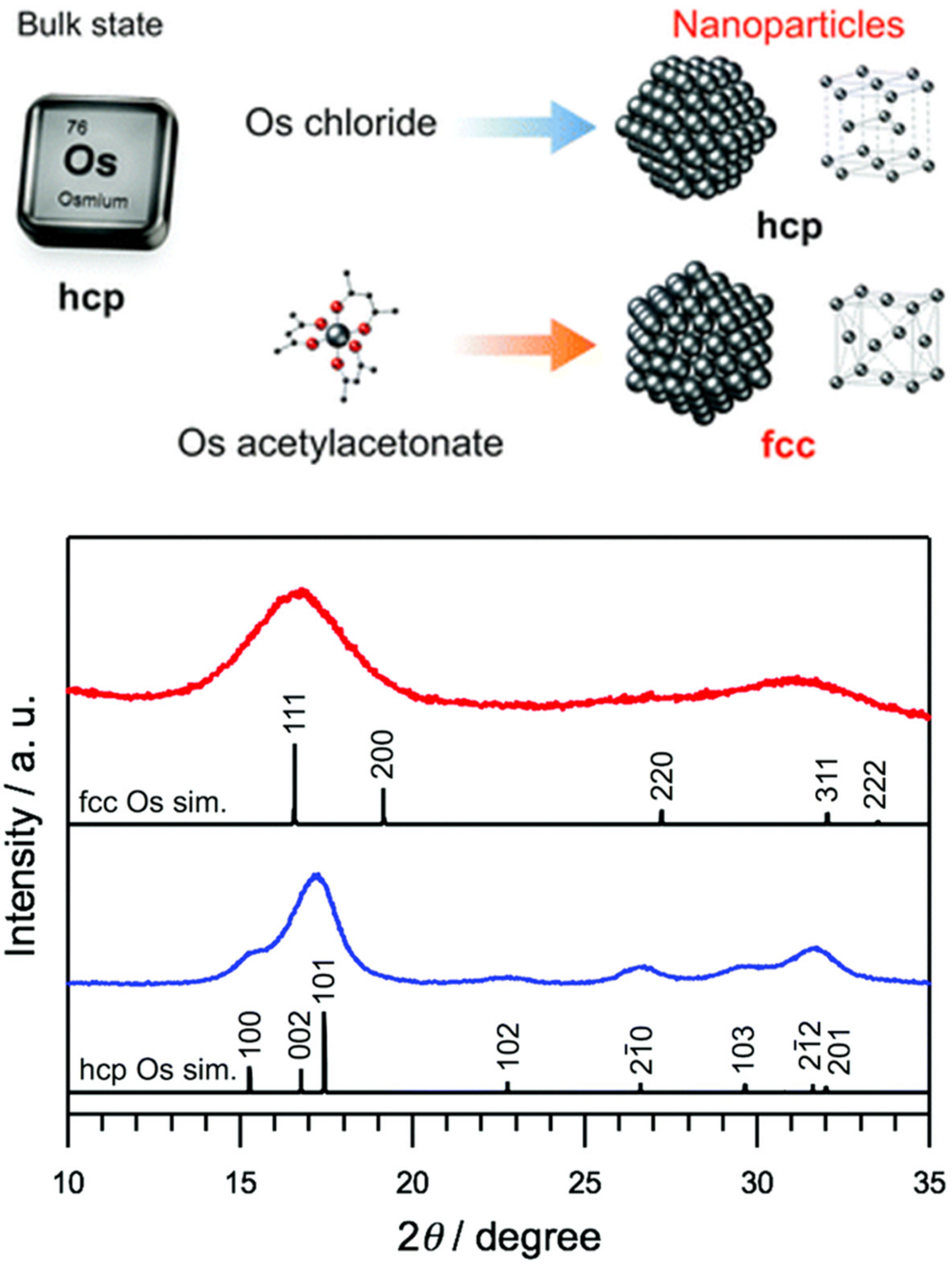

Figure 4. Tuning osmium (Os) nanoparticle structures by controlled synthesis. (Top) Schematic of the formation of face-centered cubic (fcc) or hexagonal close packed (hcp) Os nanoparticles depending on the precursor used. (Bottom) Synchrotron X-ray diffraction (XRD) patterns of Os nanoparticles synthesized using the Os(acac)$_3$ complexes (red) and (blue) OsCl$_3$, and the simulations of fcc (upper black) and hcp Os (lower black). Reproduced from 41 with permission from the Royal Society of Chemistry.

media was correlated with poor stability[84]. Nanoparticles based on Os are easy to de-alloy, e.g. Pt$_2$Os to from quasi core-shell Os@Pt for ORR in acidic media[85]. This property can be used to develop high surface area materials by de-alloying, e.g. to develop improved porous-electrodes for the oxygen evolution reaction (OER), see Figure 6[86]. Os itself is expected to show very high activity for the OER but suffer from poor stability[84].

6.2.5.3. Other applications. Os nanomaterials are less studied than other precious metals for medical applications[60] or pollution management[37]. However, Os nanoparticles found recent applications in sensing. Os nanoparticles protected by heparin as the protecting/stabilizing agent were used as a heparinase sensor[40]. Bovine serum albumin is an efficient protective shell to give Os nanoparticles an antifouling property regarding various

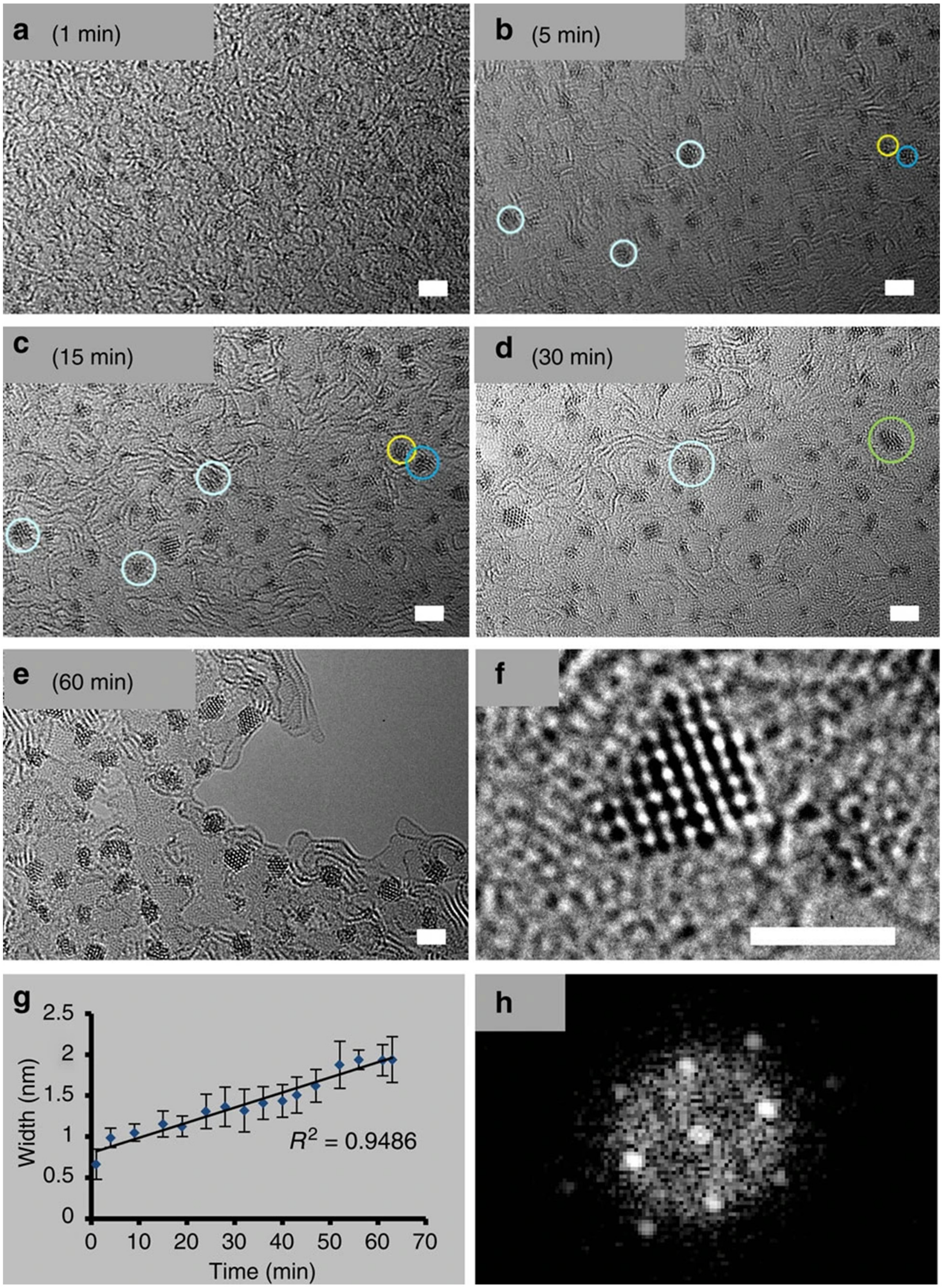

Figure 5. **Os nanoparticles as model system to study the formation and stability of nanomaterials.** (**a**–**d**) Migration of small Os clusters and their coalescence (e.g. clusters in yellow and dark blue circles merge to give crystal in green circle) over a period 1–30 min; scale bars, 2 nm. (**e**) Nanocrystals after 60 min. (**f**) Example of an Os crystal of ca. 1.5 nm, formed after 30 min of irradiation, scale bar, 1.5 nm. (**g**) Width of the clusters/crystals versus time. (**h**) Fast Fourier transform analysis of the nanocrystal shown in **f**. Reproduced from 68 with permission from Springer Nature.

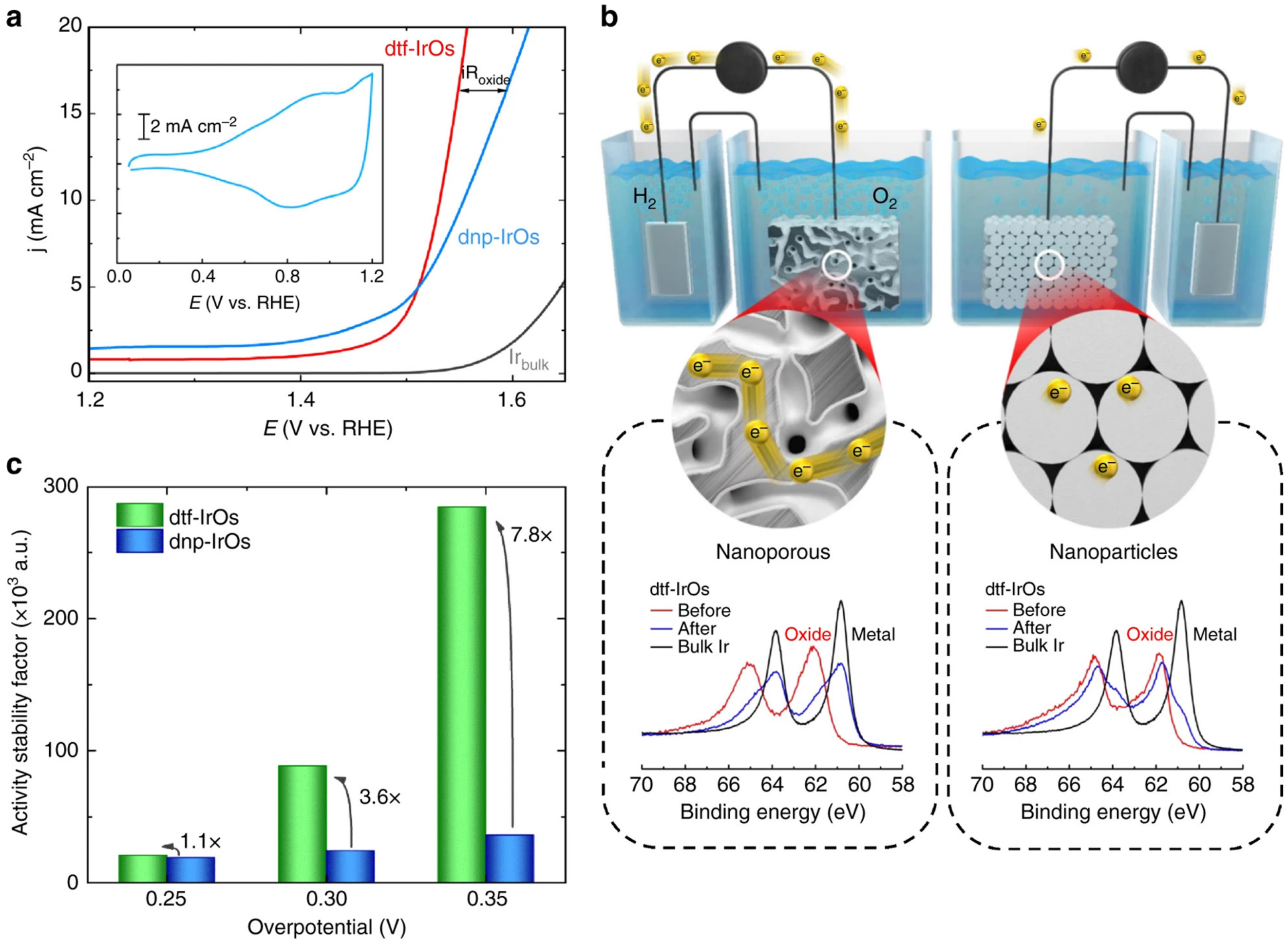

Figure 6. Electrochemical properties of Osmium (Os)-based nanomaterials: Activity-conductivity relationships in de-alloyed thin-film and nanoparticles. (**a**) Comparison between oxygen evolution reaction (OER) polarization curves for polycrystalline Iridium (Ir), de-alloyed thin film (dtf) $Ir_{25}Os_{75}$ and de-alloyed nanoparticles (dnp) $Ir_{50}Os_{50}$, indicating that conductivity limitations are observed for dnp-$Ir_{50}Os_{50}$ at higher current densities (denoted as iR_{oxide}). Inset shows the corresponding cyclic voltamograph. (**b**) X-ray photoelectron spectroscopy (XPS) sputter etching experiments demonstrating that the dtf-$Ir_{25}Os_{75}$ consists of an IrO_x shell with Ir-metallic core, in contrast to dnp-$Ir_{50}Os_{50}$ that consists entirely of IrO_x. Schematic illustrates the impact of multiple oxide-oxide interfaces (present on dnp-$Ir_{50}Os_{50}$ electrodes) on conductivity. (**c**) Change in activity-stability factor values with overpotential for dtf-$Ir_{25}Os_{75}$ and dnp-$Ir_{50}Os_{50}$ highlighting the importance of balancing activity-stability-conductivity properties of oxide materials for the OER. Reproduced from 86 with permission from Springer Nature.

ions (e.g., $Hg^{2+,}$ Ag^+, Pb^{2+}, I^-, Cr^{6+}, Cu^{2+}, Ce^{3+}, S^{2-}, etc.), saline (0–2 M), or protein (0–100 mg/mL) conditions. A colorimetric sensor was developed for H_2O_2 detection with improved properties compared to Au or Pt based sensors[87], see the illustration in Figure 7. Other examples include glucose and pyruvic acid detections[54], folic acid detection[88] colorimetric sensors for heavy metal ions discrimination ($Cu^{2+,}$ Ag^+, $Cd^{2+,}$ $Hg^{2+,}$ and Pb^{2+})[89]. Os nanoparticles also show SERS properties[36,37,76].

Theory

Less work has been performed on Os nanoparticles than Ir[90] or Pt[25] nanoparticles but some theoretical work can be found in the literature[70,91–93]. For instance, Os was suggested to be a suitable catalysts for ammonia production[94]. While being less investigated than Ir, Os_{xn} clusters were studied by density functional theory (DFT) for instance in light of their interaction with MgO for n=4,5[91]. By analogy with what is available for Ir or Pt, it can be expected that theoretical work will be valuable to clarify why small size nanoparticles are easily obtained, which might be related to the formation of 'magic number' nanoparticles with specific sizes[95] and/or sintering resistance properties[96]. Equaly theoretical work could be relevant to explore further the properties of Os based nanomaterials, in particular towards improved stability.

Os in multi-metallic nanomaterials

In addition to the examples already mentioned above, for instance in Figure 6, various alloyed nanoparticles have been

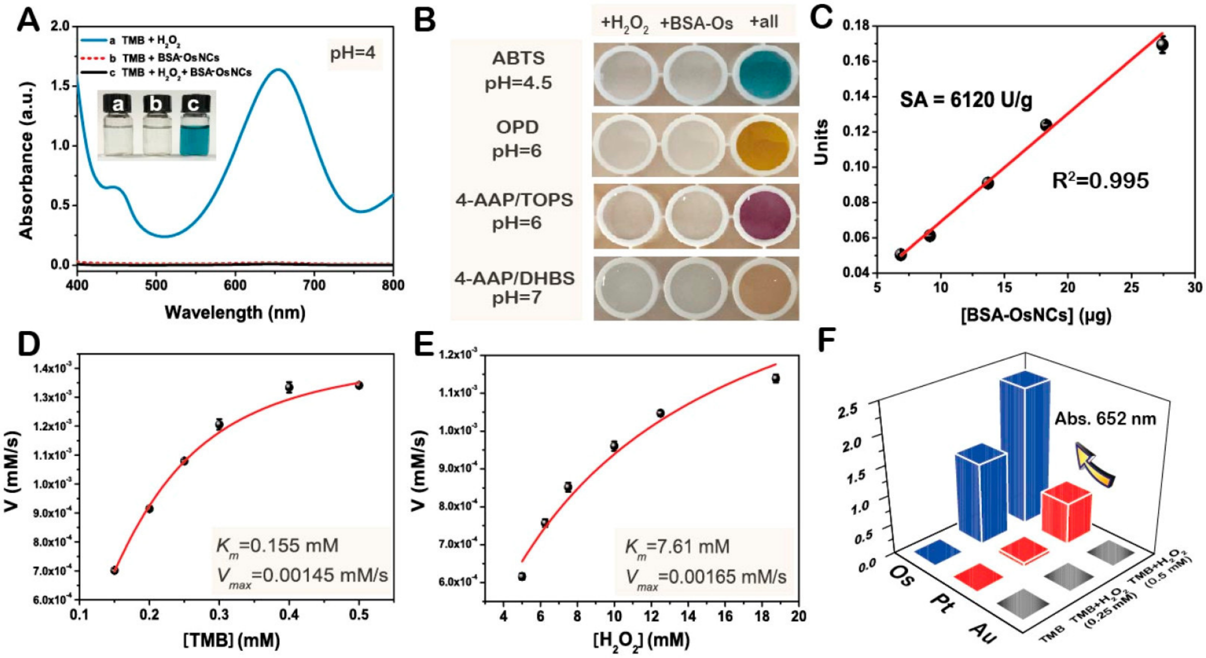

Figure 7. Osmium (Os) nanoparticles for sensing. (**A**) Ultra-violet/visible light (UV-vis)spectra of 3,3′,5,5′-tetramethylbenzidine (TMB) + H_2O_2 (0.25 mM), TMB + bovine serum albumin (BSA)–Os nanoparticles (Os content = 1 mM), and TMB + H_2O_2 (0.25 mM) + BSA–Os nanoparticles (Os content = 1 mM). Inset: Corresponding photographs. (**B**) Corresponding photographs of some peroxidase substrates catalyzed by BSA–Os nanoparticles in the presence of H_2O_2: substrate + H_2O_2, substrate + BSA–Os nanoparticles, and substrate + H_2O_2 + BSA–Os NCs. (**C**) Specific activity of BSA–Os nanoparticles. Steady-state kinetic assay of BSA–Os nanoparticles toward (**D**) TMB and (**E**) H_2O_2. (**F**) A_{652nm} of TMB, TMB + H_2O_2 (0.25 mM), and TMB + H_2O_2 (0.5 mM) catalyzed by BSA–Au nanoparticles (Au content = 1 mM), BSA–Pt nanoparticles (Pt content = 1 mM), and BSA–Os nanoparticles (Os content = 1 mM). Reprinted with permission from 87. Copyright 2022 American Chemical Society.

reported such as IrOs[14], PtOs[97], OsB_2[98], in particular for their improved mechanical properties. PdOs nanoparticles were reported as catalyst for carbon nanotube synthesis[26]. Other examples include $NiOs_4$ reported for the improved hydrogenation of cinnamaldehyde[99], PtOs for the methanol oxidation reaction[100], CuOs for the methanol oxidation reaction and ORR[101] or OsTe nanorods for cancer therapy[102].

Discussion

A range of Os nanomaterials can easily be obtained by various syntheses methods, see Table 1. In particular, a range of surfactant-free syntheses are well documented and are expected to lead to Os nanoparticles with improved properties in fields of applications like catalysis and sensing. However, the characterization of the small (<2 nm) nanoparticles obtained in most cases remains one of the bottlenecks in the study of Os nanomaterials. Relatively complex characterization techniques (not routine) are needed such as high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM)[41], or synchrotron based measurements[41], see Figure 4. For instance, X-ray diffraction technique will lead to large Bragg peaks for such small nanoparticles and most TEM equipment will not easily characterize such small nanomaterials. Also, the size range around 1 nm is at the limit of most small angle X-ray scattering (SAXS) equipment. However, recent progress in the characterization of nanomaterials[103], and in particular the increasing availability of high resolution TEM or techniques like X-ray total scattering with pair distribution function (PDF) analysis[42,104], are well suited to characterized nanocrystals. Recent advances in these techniques are expected to bring new insights into Os nanomaterial formation. The knowledge gained will be the key for improving syntheses of nanomaterials towards more functional materials. There is a regain of interest on Ir and Ir oxide nanoparticles, in great part due to high expectations on Ir as a potential catalyst for OER[105]. Ir and Os chemistry are relatively similar in the sense that they both easily lead to small size nanoparticles and clusters. This makes them ideal candidates to study nanoparticle formation and to focus on nucleation phenomena since the nanoparticle growth is moderate.

In addition, the Os materials obtained are relevant for a range of applications. In particular, high expectations are on new or improved applications in catalysis and medicine. An example of emerging opportunity is for instance the possibility to investigate the different catalytic properties of *fcc* or *hcp* Os nanoparticles, see Figure 4, largely unexplored to date.

Finally, it is expected that the interest on iridium[90] will trigger increasing interest in Os nanoparticles, which in turn will enable further exploration of Os chemistry. However, for long term applications recycling is an important issue to address[106], in particular in light of the relatively poor stability of Os in application like electrochemical energy conversion[84]. In this respect, the role and stability of Os in increasingly studied bimetallic[86] and even high entropy alloys[107] is also an opening area of research.

Conclusions

Despite a limited knowledge on the actual formation mechanism of Os nanoparticles, several approaches lead to simple syntheses of Os nanoparticles. The very small size *circa* 1–2 nm of most Os nanoparticles suggests that a range of reported syntheses probably can be simplified, *e.g.* avoiding the use of any surfactants or high temperature. Relatively high concentration of precursors can be used and still lead to small size nanoparticles which is a promising feature for future scaling. The obtained OsO_x nanoparticles already proved to be relevant for a wide variety of applications in particular as active materials in catalysis or as templating agents. (Re) Emerging areas of application include chemical synthesis[79], sensing[89] or medical applications[60].

Data availability

No data are associated with this article

Ethics and consent

Ethical approval and consent were not required.

Authors contribution

Jonathan Quinson: Conceptualization; Formal Analysis; Funding Acquisition; Investigation; Methodology; Project Administration; Visualization; Writing – Original Draft Preparation; Writing – Review & Editing

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PubMed Abstract | **Publisher Full Text**

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Publisher Full Text

106. Chen Y, Qiao QY, Cao JZ, *et al.*: **Precious metal recovery.** *Joule.* 2021; **5**(12): 3097–3115.
Publisher Full Text

107. Miracle DB, Senkov ON: **A critical review of high entropy alloys and related concepts.** *Acta Materialia.* 2017; **122**: 448–511.
Publisher Full Text

Open Peer Review

Current Peer Review Status: ✓ ✓

Version 2

Reviewer Report 02 August 2022

https://doi.org/10.21956/openreseurope.16220.r29820

✓ **Michael Nolan**

Tyndall National Institute, University College Cork, Cork, Ireland

The author has given very good responses to the original review comments and improved the original submission.

I am very happy to recommend acceptance of this interesting submission.

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: First principles simulations, nanoparticles and nanostructures, surface chemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Version 1

Reviewer Report 25 July 2022

https://doi.org/10.21956/openreseurope.15760.r29489

✓ **Shaojun Guo**

School of Materials Science and Engineering, Peking University, Beijing, China

Comments to the Authors
In this work, Quinson and co-authors reviewed the recent advances in the syntheses and applications of Os and Os-based nanoparticles. They first summarized several important synthesis methods of Os-based nanomaterials. Then, several key applications of Os-based catalysts were introduced, such as chemical synthesis, electrocatalysis and medical applications, etc. This review is logical and well-organized, and provides a valuable reference for the future design of advanced Os-based nanomaterials. In view of the timely summary/highlight and importance of this work, I recommend its indexing, only after a minor revision to address the following concerns.

1. There are too many keywords.

2. The authors proposed that Os-based materials present unique features compared to other precious metals. What are these unique features?

3. It is pointed out that the nanoparticles with very small sizes are difficult to characterize. However, I think this is no longer challenging, because many technologies have been used to characterize their structures, even some atomically dispersed catalysts, such as atomic-resolution aberration-corrected scanning transmission electron microscopy.

4. Some possible trends and challenges for future advanced research directions should be included at the end of this manuscript.

5. In **Figure 4**, there are two-phase structures for Os nanoparticles (*fcc* and *hcp*). The influence of two kinds of Os on electrocatalysis should be mentioned.

Is the topic of the review discussed comprehensively in the context of the current literature?
Yes

Are all factual statements correct and adequately supported by citations?
Yes

Is the review written in accessible language?
Yes

Are the conclusions drawn appropriate in the context of the current research literature?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: Electrocatalysis

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard.

Author Response 29 Jul 2022

Jonathan Quinson

I would like to thank the reviewer for his/her/their time to review the work and valuable comments. Answers to the comments are below:

1. The number of 8 keywords is following the recommended numbers by the Open Research Europe guidelines: https://open-research-europe.ec.europa.eu/for-authors/article-guidelines/science-technology-and-medicine/reviews/#keywords.

2. I understand that the reviewer refers here to the wording in the abstract. The wording is kept general to fit the abstract requirements. These unique features are somehow specified in the rest of the sentence ‘catalysis or sensing for instance’ and detailed all along the review. It is also stressed later that Os is one of the densest metal known. These unique features can be summed up as the different physico-chemical properties highlighted in the review, such as small sizes, and the relevance for specific applications detailed in the *Applications* section, such as catalysis, medical applications, etc.

3. The reviewer is right, and certainly how small a nanoparticle must be to start being ‘challenging’ to characterize depends on many factors. In particular, the type of equipment available to a research group will be a critical factor. However, it can be safely considered that the resolution of most transmission electron microscope (TEM) starts being limited for nanomaterials less than 1-2 nm. And certainly, high resolution TEM (HRTEM) and more advanced scanning transmission electron microscopy (STEM) are (fortunately) increasingly routine equipment. The increasingly availability of these characterization techniques is indeed expected to bring increasingly new insights into atomically structured materials.

   The comments made here were maybe to be understood considering the historical development of precious metal nanomaterial studies. As reported in *Figure 1*, Ag and Ag nanomaterials have been the most studied. This is, I believe, in great part due to their well-defined plasmonic properties which makes it possible to study the nanomaterials (and even estimate size) by simple techniques such as UV-vis. Also, a range of synthetic methods allow to form nanomaterials with a size above 10 nm, relatively easy to characterize with most TEM equipment. In contrast Pt, Pd tend to lead to smaller nanoparticles, say 2-10 nm, across various synthetic approaches, and so are less simple to characterize. Further comes Ru, Rh, Ir and Os which tend to lead to even smaller nanoparticles. The rough relationship ‘larger size correlates to larger number of research studies’ might be in part due to the facility to study relatively larger nanoparticles.

   I agree with the reviewer that the bottleneck related to characterization is maybe less challenging to date, but it still accounts for the fact that there are fewer studies on Ir or Os nanoparticles. Hence, there are high expectations on new discoveries on the related materials, now that this bottleneck is at least partially alleviated, as stressed in the second paragraph of the *Discussion* section.

4. A generic statement can be found in the *Discussion* section. This section has been re-shaped into four paragraphs and not two, to best stress future directions of research on both fundamental aspects of nanoparticle formation (and the related

characterization) and more applications. An example of an emerging new opportunity is given for catalysis, considering the comment (5) from the reviewer.

5. The reviewer is right, and this has been stressed better now in the revised version of the work: " An example of emerging opportunity is for instance the possibility to investigate the different catalytic properties of fcc or hcp Os nanoparticles, see *Figure 4*, largely unexplored to date " has been added.

Competing Interests: No competing interests were disclosed.

Reviewer Report 20 June 2022

https://doi.org/10.21956/openreseurope.15760.r29491

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Michael Nolan
Tyndall National Institute, University College Cork, Cork, Ireland

In this submission the authors presents a review of Os and OsOx nanoparticles focussing on their synthesis and applications.

Overall, the review is interesting and brings together work on a metal that receives much less attention than other precious metals.

I have some comments that I hope can enhance the submission.

1. Some comments on aspects of the language:

   Introduction "along the years" can be replaced by "over many years" (or similar)

   Page 4 "is to easily lead to relatively small"

2. Introduction: Is Os the densest metal or element?

3. Table 1 caption: add "synthesis" at the end of the caption text. Is there a chemical formula for the "Home-made" complex?

4. Author mentions a challenge with the ALD of Os nanoparticles, that is formation of toxic OsO_4. Did the ALD use an oxygen source? A H_2 plasma could be one option to reduce to Os metal.

5. Page 7 mentions how different Os precursors can produce different structured

nanoparticles - do the original papers have any discussion on the origin of this difference. For me stating "role of ligands that can stabilise a specific facet" is not sufficient.

6. I may have missed it, but given that Os appears to make small (2 nm) nanoparticles, can the author make some discussion on the origin of this?

7. The theory part is probably much too short to be of real value. The author can either remove it or expand to give some more details.

8. In multimetallic systems, is the role of Os described in the literature? What value is there in making Os alloys for chemistry?

Is the topic of the review discussed comprehensively in the context of the current literature?
Partly

Are all factual statements correct and adequately supported by citations?
Yes

Is the review written in accessible language?
Yes

Are the conclusions drawn appropriate in the context of the current research literature?
Yes

Competing Interests: No competing interests were disclosed.

Reviewer Expertise: First principles simulations, nanoparticles and nanostructures, surface chemistry

I confirm that I have read this submission and believe that I have an appropriate level of expertise to confirm that it is of an acceptable scientific standard, however I have significant reservations, as outlined above.

Author Response 29 Jul 2022

Jonathan Quinson

I would like to thank the reviewer for his/her/their time to review the work and the comments provided to improve the work. Here are the answers to the points above:

1. The language-related matters have been improved.

2. Os is the densest metal (Girolami, G.S. Osmium weighs in. *Nat Chem* 2012, 4, 954-954, DOI:10.1038/nchem.1479). Also, it is among the densest naturally occurring elements.

3. The caption of Table 1 has been corrected in the new version by adding: "Table 1. Examples of literature on osmium oxide (OsO_x) nanoparticle synthesis and

applications”

4. There is certainly a chemical forumal for the ''Home-made'' complex, given in the main text, but in light of the overview provided, we do not wish to complicate the Table and hope that interested readers will refer to the relevant literature.

   These complexes are for instance:
   [Os(η6-p-cym)(1,2-dicarba-closo-dodecarborane-1,2-dithiolato)]
   [Os(η6-p-cym)(1,2-dicarba-closo-dodecarborane-1,2-dithiolato)(triphenylphosphine)

5. The comment from the reviewer was: *''Author mentions a challenge with the ALD of Os nanoparticles, that is formation of toxic* OsO_4*. Did the ALD use an oxygen source? A* H_2 *plasma could be one option to reduce to Os metal.''* This is a fair point raised by the reviewer. In the specific study referred to where ALD was used, oxygen was used as co-precursor (Hämäläinen J, Sajavaara T, Puukilainen E, et al.: Atomic Layer Deposition of Osmium. *Chem Mater.* 2012;24(1):55–60, DOI: 10.1021/cm201795s). I am not familiar enough myself with the ALD requirements but the suggestion of the reviewer makes sense. I guess this is one of the many aspects of Os chemistry still to be explored.

6. The comment from the reviewer was: *''Page 7 mentions how different Os precursors can produce different structured nanoparticles - do the original papers have any discussion on the origin of this difference. For me stating "role of ligands that can stabilise a specific facet" is not sufficient.''* The original paper (Wakisaka T, Kusada K, Yamamoto T, *et al*.: Discovery of face-centred cubic Os nanoparticles. *Chem Commun*. 2020;56(3):372–374, 31808775, DOI: 10.1039/c9cc09192k) certainly does discuss this. The discussion has now be completed: by adding: ''A recent work showed that face-centered cubic (*fcc*) nanoparticles instead of the expected hexagonal close packed (*hcp*) structure could be obtained by careful choice of the precursor, reducing agent and solvent, see illustration in *Figure 4*. Iridium is the neighbour transition metal of Os and adopts the *fcc* structure. The difference in total energy between the *hcp* and *fcc* structures of Os is expected to be small and so it should be possible to obtain *fcc* Os nanoparticles. In presence of ethylene glycol and PVP using Os acetylacetonate ($Os(acac)_3$), *fcc* nanoparticles were obtained whereas *hcp* nanoparticles were obtained with $OsCl_3$ in water using $NaBH_4$ as reducing agent [41]. The change in structure is attributed to the role of the acac ligand that can stabilize the nearest-neighbour Os–Os bond length (ca. 2.67 Å) in a close-packed plane of Os, that is close to the O–O length (2.74–2.93 Å) of the acac ligand. This leads to nanoparticles with a different crystal structure.''

7. To the best of my knowledge, there is no definite framework to explain why Os nanoparticles are easily obtained with small sizes, although it is a very clear trend in the literature (Hirai H, Nakao Y, Toshima N: Preparation of Colloidal Transition Metals in Polymers by Reduction with Alcohols or Ethers. *J Macromol Sci Chem.* 1979; A13(6):727–750, DOI: 10.1080/00222337908056685). Just like for other transition metals, it is very likely that ‘magic number’ nanoparticles are stable and can be obtained. The open question is the driving force probably differing for different

metals that seem to lead to some of the magic clusters more than others (smaller one or larger ones depending on the metal, see Reference / comments 42 in Watzky, M.A.; Finke, R.G. Nanocluster size-control and "magic number" investigations, experimental tests of the "living-metal polymer" concept and of mechanism-based size-control predictions leading to the syntheses of iridium(0) nanoclusters centering about four sequential magic numbers. *Chem. Mater.* 1997, 9, 3083-3095, DOI:10.1021/cm9704387). The best analogy to propose an explanation to the observed small size of Os nanoparticles is probably to compare with the neighbor element Iridium, for which it has been suggested that some small structures are so stable that the nanoparticles will be resistant to sintering (Lu, J.; Aydin, C.; Browning, N.D.; Wang, L.C.; Gates, B.C. Sinter-Resistant Catalysts: Supported Iridium Nanoclusters with Intrinsically Limited Sizes. *Catal. Lett.* 2012, 142, 1445-1451, DOI:10.1007/s10562-012-0928-8). As far as I know, this property has not been fully explored and explained for osmium. This discussion comes relevant together with the comment (8) from the reviewer.

8. The reviewer is right that the theory part is relatively scarce. Especially when comparing with what can be found on Iridium (Quinson, J. Iridium and IrO_x nanoparticles: an overview and review of syntheses and applications. *Adv Colloid and Interface Sci.* 2022, 303, 102643, DOI:10.1016/j.cis.2022.102643). In light of this ‘lack’ of theoretical studies, this section is now including comments along the line of the answer made on comment (7) from the reviewer: lack of explanation of the small size of the Os nanoparticles observed across the literature. This now reads as follows: ''Less work has been performed on Os nanoparticles than Ir [90: Quinson, J. Iridium and IrO_x nanoparticles: an overview and review of syntheses and applications. *Adv Colloid Interface Sci*. 2022, 303, 102643, DOI:10.1016/j.cis.2022.102643] or Pt [25: Quinson J, Jensen KMØ: From platinum atoms in molecules to colloidal nanoparticles: A review on reduction, nucleation and growth mechanisms. *Adv Colloid Interface Sci.* 2020;286:102300. 33166723, DOI: 10.1016/j.cis.2020.102300] nanoparticles but some theoretical work can be found in the literature [70, 91-93] . For instance, Os was suggested to be a suitable catalyst for ammonia production [94]. While being less investigated than Ir, Os_n clusters were studied by density functional theory (DFT) for instance in light of their interaction with MgO for n=4,5 [91]. By analogy with what is available for Ir or Pt, it can be expected that theoretical work will be valuable to clarify why small size nanoparticles are easily obtained, which might be related to the formation of ‘magic number’ nanoparticles with specific sizes [95: Watzky, M.A.; Finke, R.G. Nanocluster size-control and "magic number" investigations, experimental tests of the "living-metal polymer" concept and of mechanism-based size-control predictions leading to the syntheses of iridium(0) nanoclusters centering about four sequential magic numbers. *Chem. Mater.* 1997, 9, 3083-3095, DOI:10.1021/cm9704387] and/or sintering resistance properties [96: Lu, J.; Aydin, C.; Browning, N.D.; Wang, L.C.; Gates, B.C. Sinter-Resistant Catalysts: Supported Iridium Nanoclusters with Intrinsically Limited Sizes. *Catal. Lett.* 2012, 142, 1445-1451, DOI:10.1007/s10562-012-0928-8]. Equally theoretical work could be relevant to explore further the properties of Os-based nanomaterials, in particular towards improved stability."

9. Comment from the reviewer: ''*In multimetallic systems, is the role of Os described in the literature? What value is there in making Os alloys for chemistry?''* This is once more a very open question. Most studies will not consider Os as an alloying element due to the risk of Os leaching, for instance for the OER (Danilovic N, Subbaraman R, Chang KC, *et al*.: Activity-Stability Trends for the Oxygen Evolution Reaction on Monometallic Oxides in Acidic Environments. *J Phys Chem Lett.* 2014;5(14):2474–2478. 26277818. DOI: 10.1021/jz501061n). Also forming porous materials by Os leaching seems an expensive strategy, although it has shown to bring useful features such as higher OER activity in some cases (Kim YT, Lopes PP, Park SA, *et al*.: Balancing activity, stability and conductivity of nanoporous core-shell iridium/iridium oxide oxygen evolution catalysts. *Nat Commun.* 2017;8(1):1449. 29129907. DOI: 10.1038/s41467-017-01734-7 5682288). The lack of consideration for Os can also come from the related toxicity and risk to form OsO_4. Finally, a generally small number of reports, and even fewer theoretical reports as highlighted in the answer to comment (7), accounts for the scarcity of rational arguments to use Os in general, and in bi/multi metallic in particular. Nevertheless, the activity of Os for catalytic applications, e.g. for the OER, is very promising if the stability issues can be addressed. In this respect, the range of opportunities offered by developing Os based materials is still to be explored. In this regard, the emerging interest around high entropy alloys (Miracle, D.B.; Senkov, O.N. A critical review of high entropy alloys and related concepts. *Acta Materialia* 2017, 122, 448-511, DOI:10.1016/j.actamat.2016.08.081) might bring new highlights in the properties of Os-based nanomaterials and this is now stressed more in the manuscript with the relevant new references here mentioned: Finally, it is expected that the interest on iridium [90: J. Iridium and IrO_x nanoparticles: an overview and review of syntheses and applications. *Adv Colloid Interface Sci.* 2022, 303, 102643, DOI:10.1016/j.cis.2022.102643] will trigger increasing interest in Os nanoparticles, which in turn will enable further exploration of Os chemistry. However, for long term applications recycling is an important issue to address [106], in particular in light of the relatively poor stability of Os in application like electrochemical energy conversion- [84]. In this respect, the role and stability of Os in increasingly studied bimetallic [86: Kim YT, Lopes PP, Park SA, *et al.*: Balancing activity, stability and conductivity of nanoporous core-shell iridium/iridium oxide oxygen evolution catalysts. *Nat Commun.* 2017;8(1):1449. 29129907, DOI:10.1038/s41467-017-01734-7 5682288] and even high entropy alloys [107: Miracle, D.B.; Senkov, O.N. A critical review of high entropy alloys and related concepts. *Acta Materialia* 2017, 122, 448-511, DOI:10.1016/j.actamat.2016.08.081] is also an opening area of research.

Competing Interests: No competing interests were disclosed.