JOHNSON MATTHEY
TECHNOLOGY REVIEW

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Radiolytic Conversion of Platinum, Rhodium, Osmium and Palladium Salts into Metal Coatings and Metal Nanoparticles

Using intense gamma ray irradiation of precious metal salts to synthesise nanoparticles

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We herein report on the effect of gamma ray radiation on platinum, osmium, rhodium and palladium salt solutions for synthesis of nanoparticles. Pt, Os, Rh and Pd salt solutions were exposed to intense gamma ray irradiation with doses varying from 70 to 120 kGy. The metal ion salt solutions were easily converted into metal nanoparticles using this radiolysis method. The radiolytic conversion effect produced metal nanoparticles suspended in solution. For Pt, Pd and Rh a metal coating on the edges of the polypropylene tube used as a container was unexpectedly observed but not for the Os solution. X-Ray diffraction (XRD) and high resolution transmission electron microscopy (HRTEM) analyses confirmed that both the coating and the metal nanoparticles correspond to the pure metal coming from the reduction of the initial salt. Quantitative analysis of the XRD patterns shows information about the size and stress of the converted metals. The production of a metal coating on polypropylene plastic tubes by gamma ray irradiation presents an interesting alternative to conventional techniques of metal deposition especially for coating the inner part of a tube.
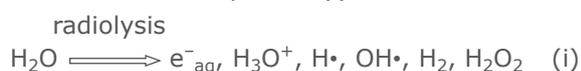
1. Introduction

Plastic materials are omnipresent in our daily life and are used in many industrial areas such as packaging, microelectronics, medical devices, automobile parts or simply as plastic bags. In many high technology applications, plastics cannot be used on their own as they do not meet the necessary requirements for expected applications. Metallisation is a way to modify

the surface of plastics for aesthetic, mechanical, biocidal and electrical purposes (1). The packaging and microelectronics industries are major users of metal-coated plastics. Metallisation can increase their gloss and reflectivity but also provide barriers for ultraviolet (UV) light degradation and enhance plastics' physical properties. Properties, such as abrasion resistance and electric conductivity, which are not innate characteristics of plastic, can be produced through metallisation. To metalise a piece of plastic common methods such as vacuum metallisation, arc and flame spraying or plating are utilised (2–5).

In this paper, we present an alternative method based on the use of intense gamma ray irradiation of metal salt aqueous solutions using a radiolysis method. This method was initiated in the 1980s by the pioneering work of Belloni and Delcourt's group using the reducing radicals produced in water radiolysis and the method was applied to some noble metals (6–9). Deposits of metal clusters were also obtained on smooth transparent tin(IV) oxide (SnO_2) and indium tin oxide (ITO) electrodes (10).

This study is focused on the radiolysis of platinum group metals (pgms) that are far less studied given their high price compared to gold or silver. Four metals were chosen in this group: Pt, Os, Rh and Pd (11–13). The radiolytic conversion of metal salt solutions into metal nanoparticles is a very well-known process of great interest as it does not necessitate the use of polluting solvents (14). It is indeed a versatile and powerful way to synthesise metal nanoparticles of controlled size and shape with the possibility to synthesise bimetallic nanoparticles and composite materials (15–20). The main advantage of radiolysis is that it operates in very simple physico-chemical conditions (room temperature, absence of contaminants, diluted aqueous solutions). During radiolysis the reducing agents are either radicals or solvated electrons that are generated by solvent excitation. The choice of the absorbed dose is critical in order to control the cluster size and crystal structure by precise modification of nucleation and growth steps particularly for multi-metal clusters (21–23). The primary effects of the interaction of high-energy gamma photons with a solution of metal ions are the excitation and ionisation of the solvent. The different reactions that are observed are well explained (24, 25). In particular, water can produce upon irradiation a series of reducing and oxidising agents as shown in Equation (i):

$$H_2O \xrightarrow{\text{radiolysis}} e^-_{aq}, H_3O^+, H\bullet, OH\bullet, H_2, H_2O_2 \quad \text{(i)}$$

To produce metal nanoparticles from metal salt solutions, the well-known reducing agents are e^-_{aq} and H•. Unfortunately, the production of hydroxyl radicals OH• hampers the efficiency unless some specific hydroxyl scavenger such as isopropanol is used. Note that as pointed out in the early research studies (25, 26), the free radical $(CH_3)_2C\bullet OH$ produced by scavenging has the peculiar property of being a strong reducing agent and also contributes to the reduction of metal ions (27).

Radiolysis has been widely used to produce gold and silver nanoparticles. A number of studies have been conducted to investigate these metal nanoparticles using UV-visible spectroscopy with the aim of analysing their plasmonic absorption band (28–30). In other studies, gamma ray irradiation was used to trap metal nanoparticles inside polymers or porous frameworks, for instance mesoporous silica (31–33). There has also been a study of the catalytic properties of Pt nanoparticles on a glass support prepared by radiolysis (34).

However, this technique has not been reported to fabricate thick coated films on the surface of vessels in which solutions are gamma irradiated and almost nothing has been published on the reduction of Os and Rh salts by this technique (35–37). In addition, the literature on the use of highly concentrated solutions is also quite sparse very likely because of the very expensive cost of the precursors.

In this paper, we report on the reduction of metal salts solutions of precious metals (Pt, Rh, Os and Pd) which were stored inside polypropylene sealed tubes during gamma irradiation. It was observed that above a threshold of 5.0×10^{-3} M, Pt and Rh solutions yielded a shiny metal deposit on the surface of polypropylene tubes below the air-solution surface. For Os solutions, the entire propylene tube was covered with a black deposit and the intensity of the deposit increased with the concentration of the solution. This deposit is reminiscent of osmium oxide which is black and volatile (38). Pd solutions also yielded some deposit on the surface of the tubes but not as shiny as those for Rh and Pt. We present in the following the details of this experiment with some characterisation of the materials formed after gamma irradiation.

2. Materials and Methods

The salts used in this study were potassium tetrachloroplatinate (K_2PtCl_4), osmium tetroxide (OsO_4) and palladium(II) chloride ($PdCl_2$)

purchased from BDH Laboratory Chemical Division, UK, and rhodium trichloride hydrate ($RhCl_3.xH_2O$) obtained from Chemica in South Africa. Isopropyl alcohol (IPA) 95% that was used in the experiment was obtained from BDH Laboratory Chemical Division, UK, and sodium dodecyl sulfate (SDS) was obtained from Merck (Pty) Ltd South Africa.

Ionic solutions of metal salts (Pt, Rh, Os and Pd) were prepared at different concentrations (1.0×10^{-3} M, 2.5×10^{-3} M, 5.0×10^{-3} M, 7.5×10^{-3} M and 1.0×10^{-2} M).

Isopropanol was added at a concentration of 2.0×10^{-1} M in each solution to prevent OH• radicals and counterbalance the effect of solvated electrons in radiolysis. Isopropanol is a very good scavenger of such radicals. In some experiments a surfactant (SDS) was added at a weight fraction of 2%. Solutions were then poured into polypropylene tubes and sealed for irradiation with gamma rays. The tubes were 13 mm inner diameter and 100 mm long. In all experiments the amount of the prepared solutions inside each tube was fixed at 5 ml. In order to avoid the presence of dissolved dioxygen inside the solutions, each tube was further flushed with nitrogen gas for 1 min prior to the gamma ray irradiation. Irradiation was conducted using a ^{60}Co source of activity 600 Gy min^{-1}. Solutions were irradiated with 70, 90 and 120 kGy doses for a duration of about 2 to 3.3 h.

XRD experiments were performed on a PANalytical θ/θ Bragg-Brentano Empyrean diffractometer (CuKα_{1+2} radiations) equipped with a Pixe detector. XRD patterns were collected in reflection geometry either on powder spread out on a glass substrate or directly on the coated surface of the polypropylene. The X-ray tube was working at 40 kV and 30 mA. Raman spectra were recorded at room temperature in the backscattering configuration on a T64000 Jobin-Yvon (Horiba) spectrometer under a microscope with a 50× objective focusing the 514 nm line from an argon-krypton (Ar-Kr) ion laser (Coherent, Innova). HRTEM experiments were carried out on a Fei Tecnai G220 operated at 200 kV. HRTEM samples were prepared by placing a drop of irradiated solution on a copper and nickel grid, followed by drying under light for 5 min at room temperature.

3. Results and Discussion

3.1 Visual Observations

Figure 1(a) shows the tubes with different concentrations of Rh solutions after irradiation at a dose of 90 kGy. One can easily observe the remarkable appearance of a shiny metal deposit on the surface of the polypropylene tubes as soon as the concentration of Rh solution is above 5.0×10^{-3} M (tube (iii)). It is thus obvious that with the increase in concentration, there is an increase of metal deposits. The deposit is very likely the result of the conversion of Rh metal ions into metallic Rh. A threshold concentration of about $c = 5.0 \times 10^{-3}$ M is the limit above which the deposit seems to
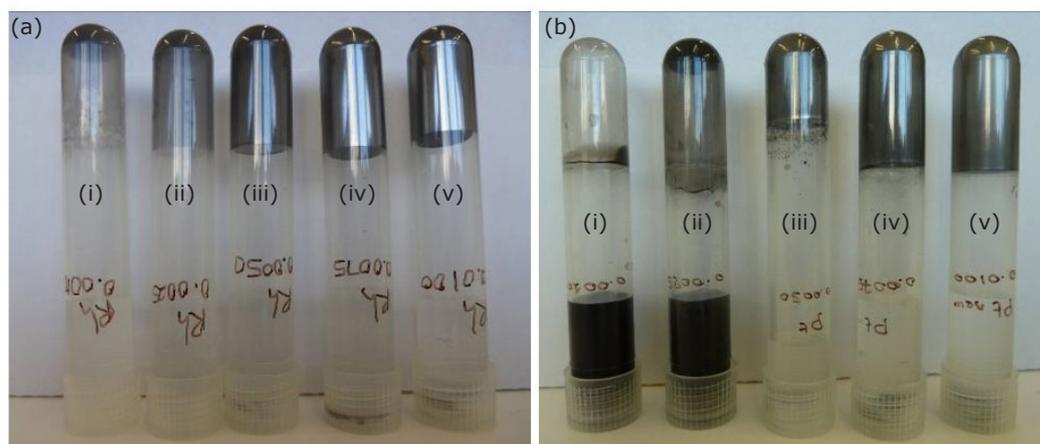

Fig. 1. Effect of irradiation on solutions of: (a) Rh and (b) Pt ions with concentrations (i) 1.0×10^{-3} M, (ii) 2.5×10^{-3} M, (iii) 5.0×10^{-3} M, (iv) 7.5×10^{-3} M and (v) 1.0×10^{-2} M irradiated at 90 kGy. Tubes are photographed vertically, head down

be continuous and complete to the naked eye. The plastic tubes did not change their colour under the effect of gamma irradiation unlike glass tubes which darkened when irradiated. At the bottom of the tubes one can see that the solutions are slightly dark evidencing the presence of small particles. There was also no evidence of any modification of the tubes when irradiated although they were likely to be sensitive to gamma irradiation.

The particles appeared not to be strongly aggregated. A similar effect was observed in the case of Pt solutions, where above 5.0×10^{-3} M, the tubes were covered with a shiny metal deposit as shown in **Figure 1(b)**, tube (iii). In addition, the interior of the tubes contained a small amount highly agglomerated black particles (Pt black). At the two lowest concentrations (1×10^{-3} M and 2.5×10^{-3} M), the solutions were observed to contain suspended particles which were certainly quite small in size and could be considered as a colloidal solution.

In order to estimate the maximum thickness of the coating, a rough calculation was made of the surface of the coating on the tube walls. In the case of the 10^{-2} M Pt solution, which was the most concentrated, it can be assumed that the thickness of the coating would be more intense. The maximum thickness of the coating (Pt film) was estimated to be 3.5 μm assuming that all the Pt was converted into the shiny deposit (which is not exactly the case as a few Pt particles were still in the solution).

It is worth noting that the solutions of Os and Pd behave very differently from those of Pt and

Rh. The solutions of Os were prepared in the same volume as those of Pt and Rh. They nevertheless produced a very significant effect during irradiation. Instead of yielding a metal film located below the air-liquid interface as is the case for Pt and Rh, Os solutions with a concentration above 5.0×10^{-3} M tubes were coated from top to bottom with a deep black deposit as shown in **Figure 2(a)**, tube (iii). This coating is very likely to be osmium(IV) oxide (OsO_2) which is known to be a dark compound and which would be a reduced form of the initial precursor since its valence is downgraded from 6 to 4 (39–41).

In the case of Pd solutions, the behaviour is again different from the other pgms, as shown in **Figure 2(b)**. It can be seen that a slight deposit formed on the part of the tube which contained the solution. However, the solution was observed to be colloidal at $c = 2.5 \times 10^{-3}$ M and very dark in colour. Above this concentration there was a yellow transparent solution forming which contained black particles. At $c = 1.0 \times 10^{-2}$ M the solution was transparent and contained aggregated black particles.

In all the above experiments, it was found that the deposit on the tube walls was extremely stable either with or without the solution kept inside the tube. Deposits were fully preserved a year after the irradiation.

The same experiments were also conducted on 5.0×10^{-3} M solutions of these metal salts, in which the SDS was added as a surfactant in order to reduce the aggregation of metal particles. As seen in **Figure 3**, the addition of SDS to the solution was observed to have a prominent effect.
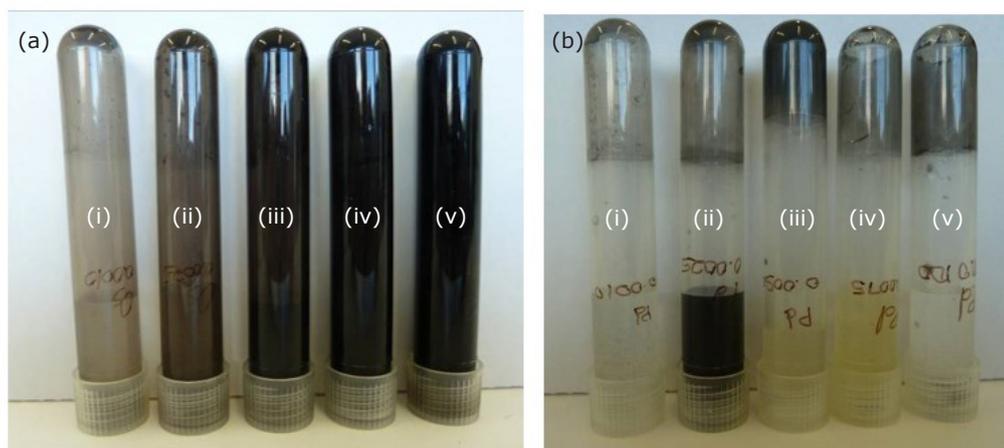

Fig. 2. Effect of irradiation on: (a) Os and (b) Pd solutions of concentrations (i) 1.0×10^{-3} M, (ii) 2.5×10^{-3} M, (iii) 5.0×10^{-3} M, (iv) 7.5×10^{-3} M and (v) 1.0×10^{-2} M irradiated at 90 kGy
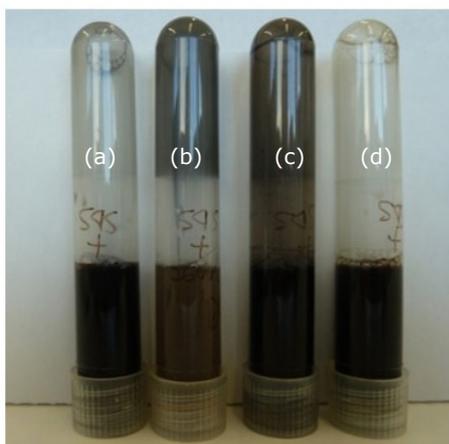
Fig. 3. Effect of irradiation on solutions (a) Pt, (b) Rh, (c) Os and (d) Pd with concentrations of 5.0×10^{-3} M with SDS added at 2% w/w and irradiated at 90 kGy

In all cases colloidal solutions were obtained with a weak deposit on the walls of the propylene tube in the case of Rh and Os. It is thus straightforward to state from a visual point of view that the effect of adding the surfactant was quite drastic. For instance Pd solutions without the surfactant yielded a yellowish colour at this concentration, in marked contrast with the dark colouration in presence of the surfactant. Similar effects were observed for Rh and Pt, while for Os it appeared that the blackening of the polypropylene tube was reduced.

Note that in agreement with our observations, in the absence of any surfactant, the precursor metal ions were mostly adsorbed on the polyethylene walls, as is known for porous supports. The low dose rate and the long irradiation time used here favour the diffusion of ions towards the walls. Moreover, it is likely that the irradiation of the support induces electrons that contribute to the reduction of adsorbed ions in contact. Then supplementary ions adsorb on the initial reduced metal layer and are also reduced *in situ*. In contrast, when the solution contains SDS, the ion binding with the surfactant is stronger than the adsorption on the polyethylene and mostly inhibits the deposit.

3.2 X-Ray Diffraction and High Resolution Transmission Electron Microscopy Analysis

The polypropylene tubes and their contents were further analysed using Raman and XRD to identify the nature of the phases formed upon irradiation.

Raman scattering using a confocal microscope was performed *in situ* (in the solution) and *ex situ* (on dried particles). No special effect of the gamma irradiation was seen on the polypropylene tube itself.

As expected from the cubic structure of these noble metals, no clear signal was measurable from either the inner part of the tube or the black particles located inside the solution in the Raman analysis.

XRD patterns of the coatings and metal nanoparticles after irradiation with gamma rays clearly revealed their metallic nature, except for Os, as shown in **Figure 4**. One can clearly see in **Figure 4** that the diffraction patterns are fully consistent with the *Fm3m* structures of bulk pgm except for the case of Os. The diffraction peaks are extremely broad in the case of Pt evidencing the fact that the size of the particles that coherently diffract is quite small. The broadening is less for Rh and even less for Pd, which might be due to the fact that in the order Pd < Rh < Pt, it is easier to reduce the ions because of four chloride ligands on $[PtCl_4]^{2-}$ that are able to stabilise small size particles (21). In the case of Os, the XRD pattern did not reveal any features showing that the deposit was mainly amorphous. A fit to the data was carried out with the Materials Analysis Using Diffraction (MAUD) program developed by Lutterrotti (42). Very good agreement can be seen between the calculated and the observed patterns. The advantage of using this program is that it allows the size of the crystallites that scatter coherently to be determined, together with the strain of the lattice. The parameters obtained reveal that the lattice parameter for Pt is very close to that of the bulk. The size of the particles corresponding in this case to the size of the domains which coherently scatter the beam is about 8.8 nm and the lattice is clearly strained.

The Pt deposit on the tube walls was also analysed by XRD. The tube was cut along its principal axis and the inner part of the tube was mounted on the stage of the XRD. It was observed that this deposit was shiny and quite fragile when subjected to scratches with tweezers. The shiny aspect of the deposit was a clear signature of its metallic nature. However when a scan in conventional θ-θ geometry was carried out, no measurable signal of the Pt deposit was obtained. The main reason was attributed to the very small thickness of this deposit that was precluding the measurement of a correct signal over noise ratio. For this reason a 2θ scan (detector scan) was performed at a fixed grazing incident angle of about 0.9º using a parallel beam coming from a
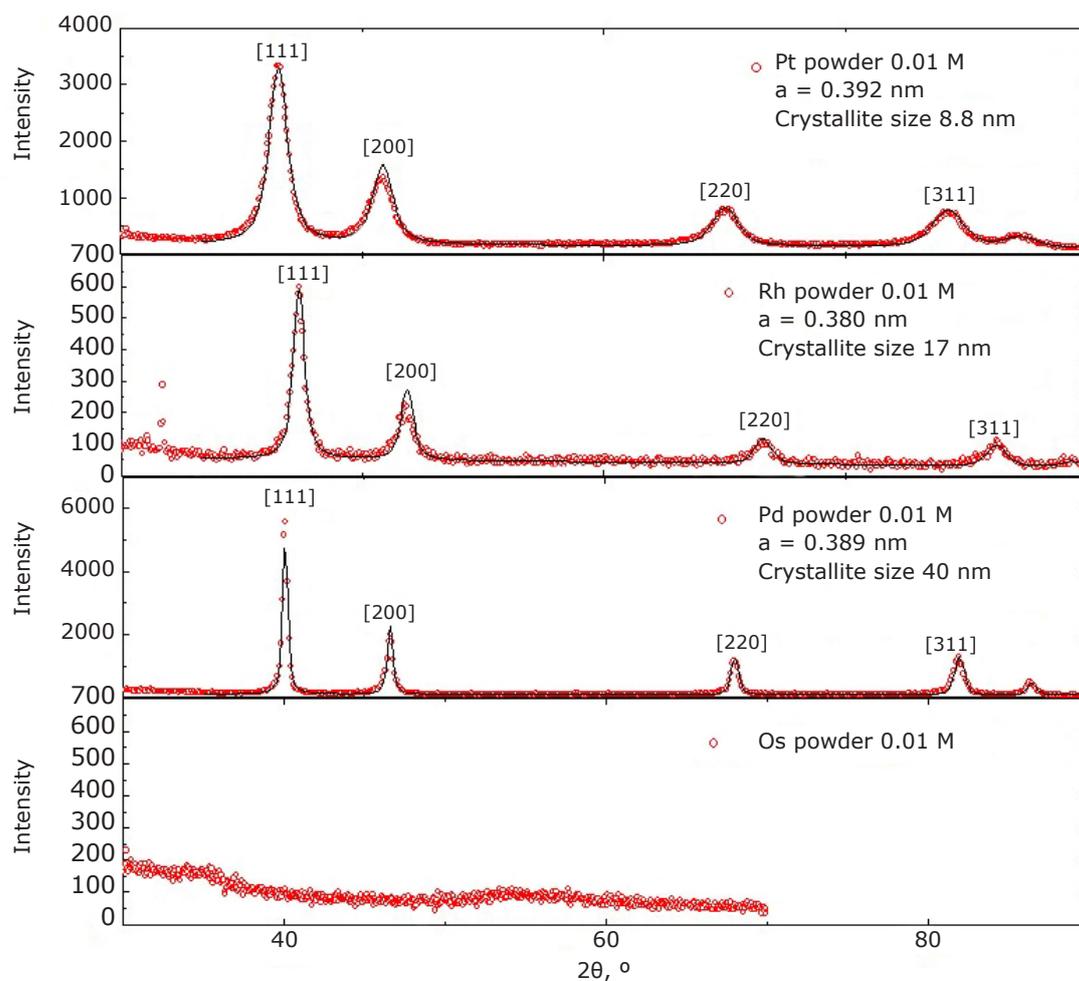
Fig. 4. XRD patterns of Pt, Rh, Pd and Os particles

W-C mirror (Empyrean diffractometer PANalytical). It was thus possible to identify all the reflections of the *Fm3m* structure, clearly evidencing that the thickness of the deposit was extremely small and that the deposit was pure Pt (see **Figure 5**). Similar conclusions could be drawn for Rh and Pd.

Note that in the case of the coating, experiments were carried out at grazing incidence and that the scattering by the tube itself was subtracted. One can see clearly the perfect concordance between the two patterns.

Table I gathers some typical information concerning the metals studied hereafter together with the values measured for some of the parameters (i.e. lattice parameters, size and strain) after refining the measurements using the MAUD Software (42).

As shown in **Figures 6–8**, HRTEM analysis of the metal nanoparticles present in the solution also complement the XRD results. It can clearly be observed in these images that particles are agglomerated.

The rings observed in the electron diffraction scattering patterns are in good agreement with the calculated *d* spacing values from Pt, Pd and Rh diffraction data from the literature. The set of *hkl* indices corresponding to these rings are shown in **Figures 6(b)**, **7(b)** and **8(b)**.

From this present study it can be confirmed that gamma ray irradiation of salt solutions containing Pt and Rh ions at dose rates above 70 kGy can be used to convert the pgm salts into metal nanoparticles in the bulk and produce a shiny metal coating on polypropylene tubes. The Pd salt solution did not yield such a shiny coating whereas the Os solution produced an intense black coating, the structure of which was found to be amorphous.
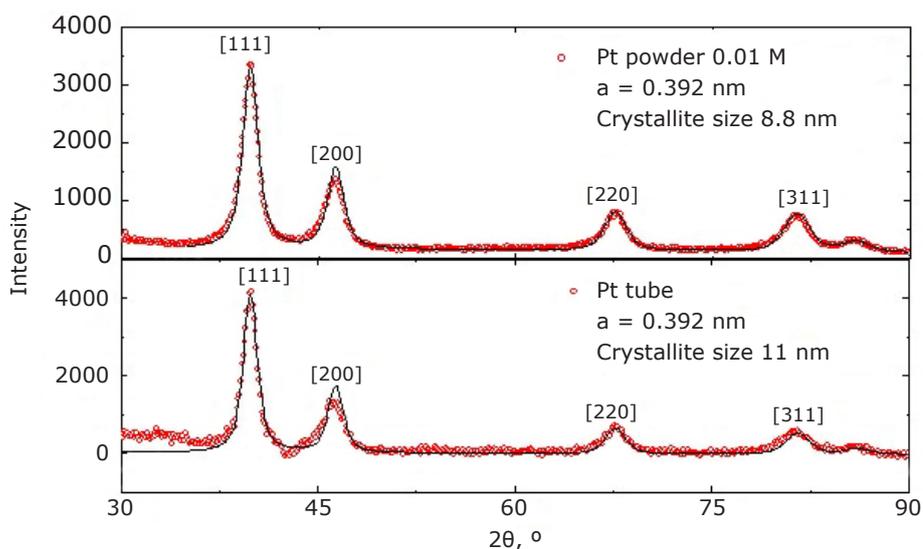
Fig. 5. Comparison between the X-ray powder diffraction patterns collected on Pt powder and on the coating of the polypropylene tube

Table I Space Groups of Platinum, Palladium, Rhodium and Osmium Together with Bulk Lattice Parameters and the Measured Values of the Lattice Parameters in this Study, the Size of the Particles in Powder and the Strain

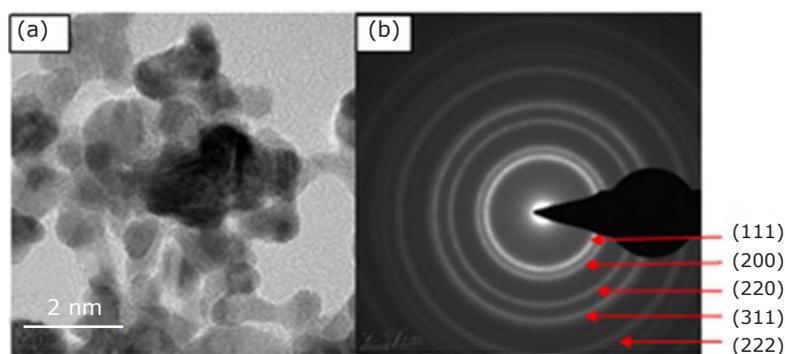| Metal	Space group	Bulk lattice parameter, a, nm	Measured lattice parameter, a*, nm	Size of particles, nm	Measured strain
Pt	*Fm3m*	0.39242	0.39222 (0.0001)	8.8 (0.2)	0.0057 (0.0002)
Rh	*Fm3m*	0.38034	0.38066 (0.0005)	16.9 (0.6)	0.0038 (0.004)
Pd	*Fm3m*	0.3807	0.38947 (0.0001)	41.7 (1.1)	0.0015 (0.0001)
Os	*P6$_3$/mmc*	a = 0.27311 c = 0.43173	N.A.	N.A.	N.A.

Fig. 6. (a) HRTEM image of Pt particles synthesised by gamma irradiation at a dose of 120 kGy; (b) selected area electron diffraction (SAED) of Pt nanoparticles
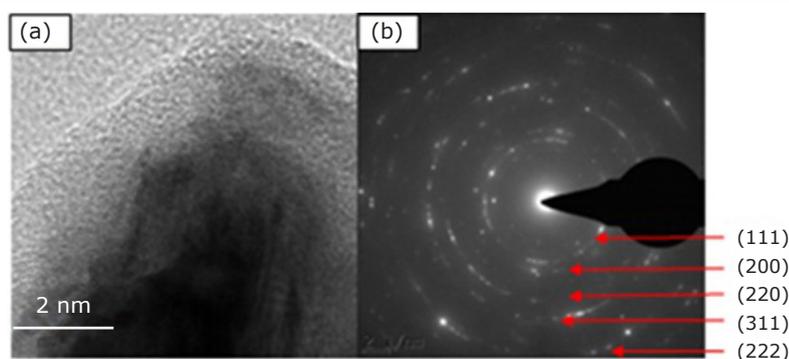
Fig. 7. (a) HRTEM image of Rh particles synthesised by gamma irradiation at a dose of 120 kGy; (b) SAED of Rh nanoparticles
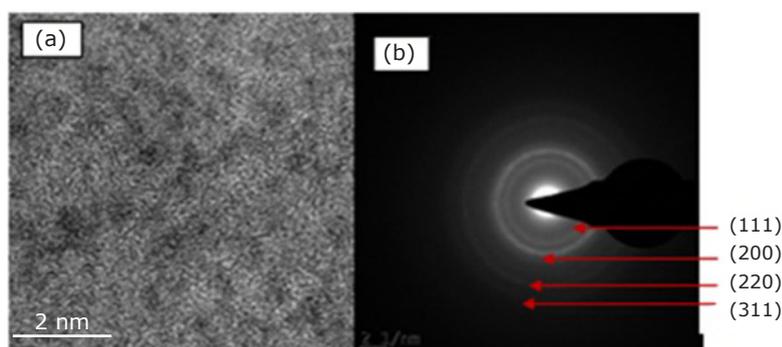

Fig. 8. (a) HRTEM image of Pd particles synthesised by gamma irradiation at a dose of 120 kGy; (b) SAED of Pd nanoparticles

4. Conclusion

The noble metal salt solutions of Pt, Os, Rh and Pd were successfully reduced into metal nanoparticles using gamma ray irradiation at doses ranging from 70 to 120 kGy and even into a metal coating of the propylene tubes, except for Pd solutions. The structure of the metal nanoparticles and the coating was ascertained by a quantitative analysis of the XRD patterns. It is shown that these patterns are fully consistent with the *Fm3m* structure of these noble metals except for Os for which it was impossible to define any crystalline structure. This study revealed that gamma irradiation can be used to produce beautiful shiny metal coatings with Pt and Rh on the inner surface of plastic tubes provided that the concentration of the initial solution is high enough (in this case $>5 \times 10^{-3}$ M). Such an effect was unexpected and is of clear interest as

an alternative to other deposition techniques such as metal evaporation or sputtering. The coating was found to be extremely stable in solution since no modification was observed even one year after irradiation. However when the tubes were cut, the coating could be easily scratched with tweezers. This was showed clearly that although the coating was stable as a function of time, the adhesion of the metal particles to the tube was not extremely good. Atomic force microscopy (AFM) studies of the coating are planned in the future to evidence the quality of the adhesion.

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Malik Maaza is a Professor, a Senior Scientist and staff member of the National Research Foundation of South Africa. He holds a PhD in neutron quantum optics from Université Pierre et Marie Curie, France, and an MSc in Photonics and lasers from Université Pierre et Marie Curie and Université Paris-Sud, France. He is the current holder of the UNESCO Africa Chair in Nanosciences and Nanotechnology. He pioneered world-class nanoscience research within the continent and at the international level. He has scientific expertise in the fields of surface and interface two-dimensional (2D)-phenomena, solar energy, neutron quantum optics specifically and neutron and X-ray scattering in general. He has authored and coauthored about 350 international peer reviewed ISI-CSI publications in reputable journals. He is the sole African author who has been invited to publish in *Physics Report* (2016 Journal Impact Factor 17.425, Clarivate Analytics 2017) and has recently coauthored a publication in Nature's *Scientific Reports* (Nature group series). He is one of the rare African scientists serving on several editorial committees of ISI-CSI international journals such as the *Journal of Materials Chemistry A* and the *International Journal of Nanotechnology*.

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