# NANOPLATINUM PREPARATION BY IRRADIATION METHODS IN MICELLAR SYSTEMS

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**Abstract**

This work deals with the preparation of platinum nanoparticles using ionizing radiation - accelerated electrons with energy 4.5 MeV produced by linear accelerator Linac-4-1200 Tesla VT Mikroel. Aqueous solutions of platinum chloride with Triton X-100 as a reducing and stabilizing agent were used. Solutions were irradiated with doses up to 20 kGy in 20 ml glass vials. Solutions containing platinum ions were colored from yellow to black color after irradiation, depending of the dose. This points platinum ions reduction and nanoplatinum formation. Irradiated solutions were monitored by UV/VIS spectrometry, photon cross-correlation spectroscopy to determine particles size and distribution, transmission electron microscopy and X-ray diffraction analysis to provide information on the forms of prepared nanoparticles. The effects of $PtCl_4$ and Triton X-100 concentrations and also dose deposited energy were studied.

**Keywords:** Nanoplatinum preparation, electron irradiation, Triton X-100, micelles

## 1. INTRODUCTION

Nanoparticles have properties which differ from those of larger particles of the same substance as effects related to particles surface increase in significance. In recent years, many methods have been developed to prepare particles with specific sizes, morphologies and composition. Metal nanoparticles in particular are valued for their many and varied applications.

Nanoplatinum usually occurs in the form of suspensions or colloids. Platinum nanoparticles have different shapes - spherical, rod-shaped, cubic or tetrahedral. Nanoparticle sizes range from 2 to 100 nm, and its size strongly depends on the method of preparation. Although nanoparticles are more or less the subject of research, they are used in the areas of catalysis, medicine and in the production of new materials of specific properties. This allows for its unique catalytic, magnetic and optical properties [1].

Regarding the catalytic properties NP are used for the reactions, such as for example hydrogen oxidation, methanol and ethanol oxidation, formic acid oxidation and oxygen reduction reaction. Regarding the catalytic properties, platinum is highly stable and has very good electrocatalytic activity in fuel cell reactions. Platinum catalysts also play a major role in chemical detection. These include, in particular, the use of platinum for the detection of carbon monoxide and oxides of nitrogen, oil refining and many others [1]. The optical properties of nanoparticle-based nanomaterials can be monitored using Raman spectroscopy. Unlike nanoparticles of other metals have a plasma peak in the visible spectrum; nanoplatinum particles have a plasma peak in the ultraviolet region around 215 nm [2].

The goal of this work is to mention the basic irradiation methods - notably electron beam, gamma radiation and UV photolysis - in which nanoplatinum can be generated from aqueous solutions of $PtC_4$ in nonionic surfactants especially in Triton X-100 and to describe some of the physicochemical properties of the particles prepared. The most notable of these properties are the effects of the initial concentration of $PtC_4$ and of the surfactant used on the subsequent concentration of nanoparticles prepared.

## 2. RADIOLYTIC PREPARATION METHODS

During radiolysis of water conventional species such as $H^+$, $OH^-$ and $H_2O_2$, as well as several species more reactive than regular chemical compounds, form [3] and are shown in equation 1. Species thus formed from water compose a majority of the products of ionizing radiation in solutions.

$$H_2O \rightarrow e_{aq}^-, H^+; {}^{\bullet}OH; H_2; H_2O_2; H^+; OH^- \quad (1)$$

For the reduction of silver ions several of these products are useful. Perhaps the best reducing agent due to its high standard redox potential is the hydrated electron ($e_{aq}^-$) with $E^0(e_{aq}^-/e^-)$ = -2.9 V. These solvated electrons are thermalized and surrounded by oriented water molecules and are highly reactive. A second, weaker reducing agent - which gains significance with decreasing pH values - is the $H^{\bullet}$ radical which forms according to the reaction in equation 5. It has a standard redox potential $E^0(H^{\bullet}/H^+)$ of -2.3 V.

$$e_{aq}^- + H^+ \rightarrow H^{\bullet} \quad (2)$$

The third highly reactive product is the hydroxyl radical $^{\bullet}OH$, which is a strong oxidizing agent. To be able to produce a reducing environment, the influence of $^{\bullet}OH$ radicals must be reduced To do this, a radical scavenger is chosen to transform the oxidizing $^{\bullet}OH$ radicals into reducing - if weak - radicals of the scavenger. The general scavenging equation is equation 6. Common scavengers include alcohols (equation 7), such as methanol, ethanol and propan-2-ol and format (equation 8).

$$OH + RH \rightarrow R^{\bullet} + H_2O \quad (3)$$

$$OH + RR'CHOH \rightarrow RR'COH + H_2O \quad (4)$$

$$OH + HCOO^- \rightarrow COO^- + H_2O \quad (5)$$

After this modification, the solvated electrons or various reducing radicals act to reduce the platinum ions.

Use ionizing radiation to induce redox reactions has the advantage of a relatively simple relation between the dose and dose rate of irradiation and those which produce nanoparticle. Changes in the dose rate can modify the size; changes in the dose up to a certain level increase the concentration [4,5].

## 3. STABILIZERS

The high surface energy of platinum nanoparticles, which opens up so many new applications, also causes them to be unstable and have a tendency to form aggregates. To prevent aggregation, nanoplatinum must be stabilized in some way. Common methods include dispersing the particles in a gel] or adding a stabilizing substance which binds to the molecule. A simple separation and stabilization method which relies on physical rather than chemical bonds is the use of surface active substances, which stabilize the nanoparticles within micelles.

Nonionic surfactants generally consist of a long polyoxide-ether chain, most commonly a polyethylene glycol either with an aliphatic and/or aromatic tail. The two surfactants used for our experiments are Triton X-100 and Brij L4 (also known under another trade name as Brij 30) and in the experiments described in this paper Triton X-100 was used. Triton X-100 is one of the trade names for 4-(1,1,3,3-Tetramethy(lbutyl)phenylpolyethylene glycol (see **Figure 1**), where the number of ethylene glycol groups averages between 9 and 10. In an aqueous solution with a pH of less than 8, it takes on the form of a symmetrical 95 700 u particle with a radius of gyration of 2.93 nm. Its critical micellar concentration is 0.2 - 0.9 $mmol.dm^{-3}$ [6], which, given its average molecular weight of 625 $g.mol^{-1}$, is equal to about 0:013 ± 0:056 w%. Brij L4 is the trade name used to refer to Tetraethylene glycol dodecyl ether [80] (see **Figure 2**). In aqueous solutions it is considerably less soluble than Triton X-100, due to its shorter ethylene glycol chain and is thus prone to forming emulsions rather than colloids. Its critical micellar concentration is about 10 $mg.dm^{-3}$ [7,8].

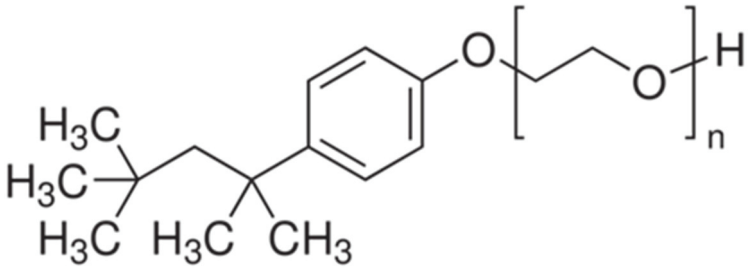


**Figure 1** Triton X-100, n = 9-10

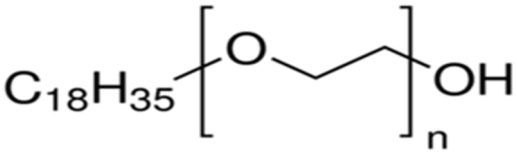


**Figure 2** Brij L4, n = 4

Nonionic polyethylene glycol type surfactants were chosen not only for their suitable stabilizing character, but also for their radiation properties. They can act as radical scavengers, forming water and a radical on the first carbon (see equation 12) much like the diols described by Billany et al. [8]. The radical is then free to reduce silver ions in solution or adsorbed on the surface of a silver nanoparticle (n = 1, respectively n > 1 in equation 13). These reactions are analogous to the reaction with glycol by Soroushian et al. [9].

$$R\text{-}OH_2CCH_2OH + OH^{\bullet} \rightarrow R\text{-}OH_2CC^{/}HOH + H_2O \quad (6)$$

$$R\text{-}OH_2CC^{/}HOH + Pt^{+} R \rightarrow {}^{\bullet}OH2CCHO + Pt^{0} \quad (7)$$

Where R = $C_{12}H_{25}$-$(OCH_2CH_2)_3$ for Brij or t-Oct-$C_6H_4$-$(OCH_2CH_2)$x and x = 8 - 9 for Triton X-100.

## 4. EXPERIMENTAL

### 4.1. Chemicals

Triton X-100 and $PtCl_4$ were purchased from Merck. All chemicals purchased were analytical grade and were used without further purification.

### 4.2. Sample Preparation

Nanoplatinum in aqueous solution of surfactant was prepared at the desired concentration (2 wt.% for Triton X-100) by adding the liquid surfactant to water and continuously mixing it until a homogenous solution was formed in the case of Triton X-100. It usually took about one hour to prepare the desired solution. Solid $PtCl_4$ was then dissolved in the continuously stirred solution. Samples were stored in the dark to shield them from the effects of UV light present in natural sunlight.

### 4.3. Electron Irradiation

A 10 mL sample of the prepared solution was then transferred into 10 or 20 mL ampoules, which were secured with parafilm. The ampoules were placed on a tray on the conveyor and irradiated with 4.5 MeV electrons from a linear accelerator with doses ranging from 1-32 kGy. The samples were placed on the tray all at once and irradiated until a sample was to be taken then irradiation resumed. If the jump between doses increased, then the dose rate was adjusted accordingly. An identical sample containing all the components except the platinum chloride was also irradiated at 24 kGy. This was then used as the standard for taking base readings

### 4.4. Instrumentation and Sample Evaluation

**UV-Vis Spectrometry.** Absorbance at certain peaks serves to describe the concentration of individual species of platinum nanoparticles. To obtain Pt spectra, the measurements were performed on a Cary 100 Conc double beam spectrometer from Varian, Inc. (measurement range 190 - 900 nm). It uses a tungsten halogen lamp for visible light and a deuterium arc as the ultraviolet source and signals are captured on a R928 photomultiplier tube. Analysis was done in the Cary WinUV control program. Samples were measured in fused silica cuvettes. Solutions were diluted with water to the concentration necessary to give an absorption in the 0 - 1 range, where the Beer-Lambert law is valid. Standards were used at the same dilution

**Photon Cross-correlation Spectroscopy**. (PCCS) in the configuration supplied by Sympatec - their NANOPHOX machine in combination with the WINDOX 5 software were used in the measurements. The NANOPHOX system uses a He-Ne laser with a wavelength of 632.8 nm with an adjustable position. Samples are kept in a thermostatic bath. In photon correlation spectroscopy the scattering of a beam of light on a particle is measured. Such scattering is used to detect the Brownian motion of particles which depends on temperature, the size and shape of the particle, as well as on other factors such as viscosity.

**Transmission electron microscopy** was used to obtain sample images that could serve to compare the particles size of the sample and also to determine the shape of nanoparticles. Nanoparticle images were taken with the JEOL JEM 3010 transmission electron microscope, which includes so-called edox (for electron dispersion spectroscopy). High concentration samples for this electron microscope were diluted with distilled water and ethanol. They were then homogenized by ultrasound. Samples were plated on a copper plate, on the carbon-coated side and plates were placed in a holder, which was then inserted into an electron microscope and then pumping of the vacuum was started. In addition, cathode heating was switched on at 2000 ° C. After the cathode was irradiated, it was possible to monitor the sample on the electron microscope shield. This image was digitized and transferred to the computer by cameras. The images were processed by Digital Micrograph.

**Rtg. structural analysis.** The measurement was carried out on a Rigaku Miniflex 600 X-ray diffractometer. The x-ray source of this device is a copper X-ray tube with a nominal output of 1 kW, cooled by water from an external cooling circuit. For detection a NaI(Tl) scintillation detector with a beryllium window on a moving arm was used. The diffraction measurements were performed in a pseudo-continuous mode in the range of 10-80°. The sample was placed in the center of the goniometer in the stationary holder (recessed plate). The measured samples were processed using the PDXL 2 program.

**Figure 3** Appearance of irradiated samples. The samples are sorted from the back to the front according to the increasing concentration: 1 mM PtCl4, 2 mM, 5 mM and 10 mM and from left to right according to the increasing dose: 0, 4, 8, 12, 16 and 24 kGy

## 5. RESULTS AND DISCUSSION

Appearance of irradiated samples is shown in the **Figure 3** Solutions containing platinum ions were after irradiation colored from yellow to black colour, depending of the dose. This points platinum ions reduction and nanoplatinum formation.

### 5.1. UV-VIS Spectrometry

UV/VIS spectra obtained by electron irradiation are in the **Figure 4**.

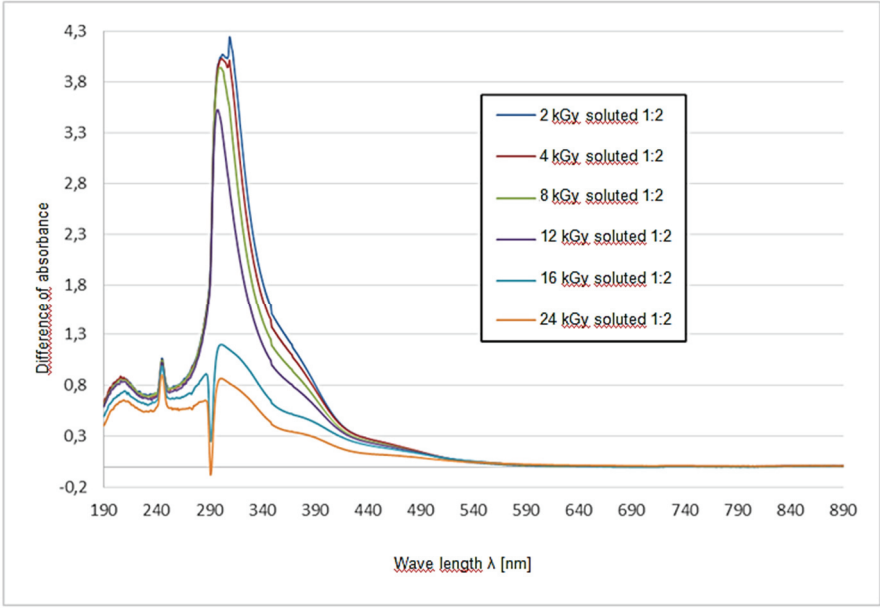


**Figure 4** UV/VIS spektra for 10 mM $PtCl_4$ solution (2 wt. % Triton X-100) irradiated by the doses 2-24 kGy

### 5.2. Photon Cross-correlation Spectroscopy

Some results obtained by PCCS are listed in **Table 1**. It concerns samples prepared from 1 mM $PtCl_4$ solution in 2 wt.% Triton X-100 irradiated by the dose 2, 4, 6 and 8 kGy were measured.t

**Table 1** Particle size of samples 1 mM $PtCl_4$ in 2 wt.% Triton X-100 irradiated by the dose 2, 4, 6 and 8 kGy

| Dose (kGy | Particle Size (nm) | kcps |
|---|---|---|
| 2 | 4.3 | 562 |
| 4 | 5.3 | 1435 |
| 6 | 4.6 | 680 |
| 8 | 4.0 | 716 |

### 5.3. Transmission electron microscopy 7

Some results obtained by TEM are in the **Figure 5**. It concerns samples prepared from 0.5 wt. % Triton X-100 + 1 mM $PtCl_4$

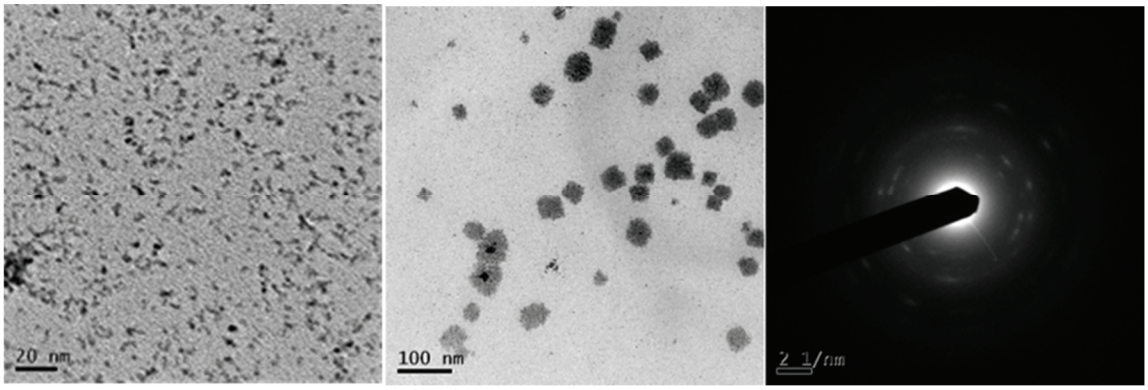


**Figure 5** Samples irradiated with a dose of 4 kGy - particle size 4.0 nm and with a dose of 6 kGy - particle size 4.6 nm. Aqueous solution of 0.5 wt. % Triton X-100 + 1 mM $PtCl_4$

### 5.4. Rentgen diffraction analysis

The resulting diffractogram is shown in the **Figure 6**. A sample containing 2 mM $PtCl_4$ in 2 wt. % Triton X-100 irradiated with a dose of 8 kGy was used. The figure shows the sample diffractogram (red line), the membrane diffractogram (green) and the resulting diffraction pattern of the sample and the membrane. According to the available database, platinum has diffraction peaks around the diffraction angles of 39.76°, 26.24° and 67.46°. In the **Figure 6** the occurrence of these peaks indicates the presence of reduced platinum $Pt^0$.

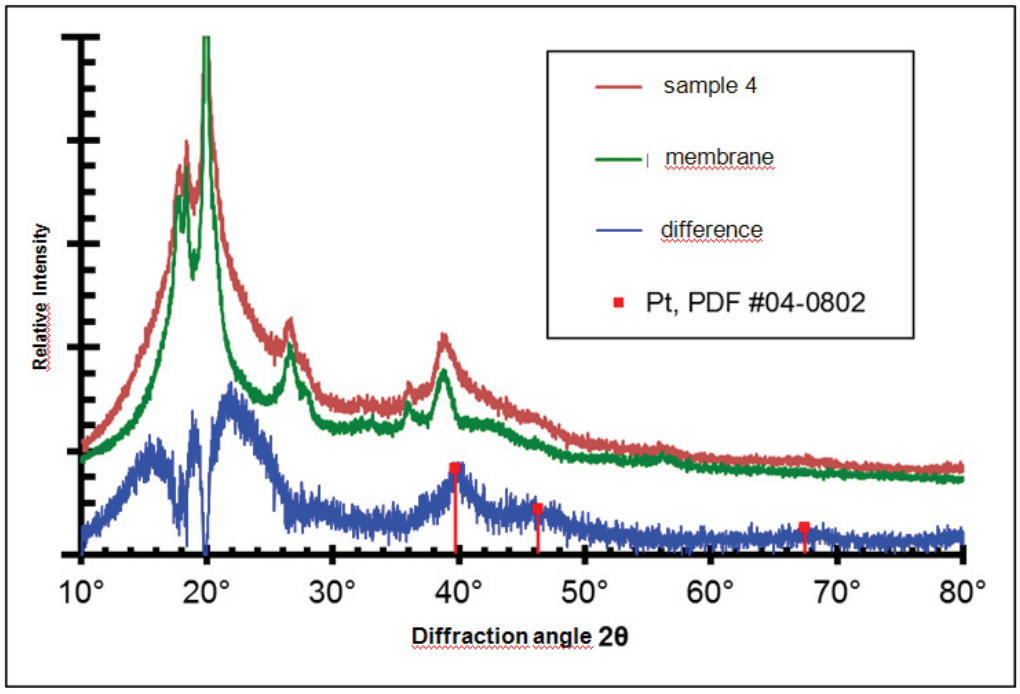


**Figure 6** The resulting diffractogram. Sample 2 mM $PtCl_4$ in 2 wt.% Triton X-100, 8 kGy

## 6. CONCLUSION

The irradiation of samples with accelerated electron changed the original colour of the solution from yellow to black. This indicates the formation of nanoplatinum.

The results of UV / VIS spectrophotometric measurements indicate that the nanoplantinum may be formed relative to the plasma peak around the wavelength of 215 nm. This peak, however, is not 100 % demonstrable due to the degradation of the UV / VIS spectrum in the UV area by the presence of Triton X-100.

Results of transmission electron microscopy and photon cross correlation spectrometry indicate the platinum nanoparticles occurrence with size within the range of several nanometers. In addition to these nanoparticles, there were also larger particles likely to occur due to the aggregation of nanoparticles in larger units. These large particles, however, occupy a minority share. X-ray diffraction analysis results the presence of platinum diffraction peaks.

These results demonstrate the possibility of radiation preparation of nanoplatinum in associative colloids represented by Triton X-100. For more accurate nanoplatinum identification, spectrum degradation in UV / VIS spectrophotometry by Triton X-100 is to be eliminated.

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