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## Formation mechanism of Pd/PVP nanoparticles: effect of ultrasonic irradiation time

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### Abstract

The effects of ultrasonic irradiation time on the palladium nanoparticles ( $Pd_n$ s) formation mechanism have been investigated using UV-Visible spectroscopy, Fourier transform infrared spectroscopy (FTIR) and transmission electron microscopy (TEM).  $Pd_n$ s colloids have been prepared by ultrasonic irradiation of  $Pd(NO_3)_2$  solutions at different irradiation times (from 30 to 180 minutes). The obtained results show that the rate of sonochemical reduction of Pd(II) ions has been found to be dependent upon the irradiation time. The kinetic of  $Pd_n$ s formation can also be correlated with the rate of sonochemical reduction of

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Pd(II) ions, as well as with the role of PVP molecules. The results suggest a three-step mechanism to describe the Pd<sub>n</sub>s formation as a function of ultrasound irradiation time. During the first step, the Pd(II) ions are rapidly reduced to Pd(0) atoms, and when the concentration of Pd(0) atoms is sufficient for nucleation, the formation of primary particles occurs which are stabilised by a maximal number of PVP molecules. During the second step, these particles grow progressively by adsorption of the Pd(0) atoms and the obtained particles are coordinated to all available PVP molecules. The third step corresponds to decrease of the bounded PVP to the particle surface and the growth of the large particles at the expense of the unstable small ones.

Keywords: Palladium nanoparticles, ultrasound irradiation, formation mechanism, UV-visible spectroscopy, FT-IR spectroscopy, TEM.

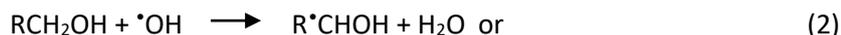
## 1. Introduction

The important technological development and the improvement of the investigation means allow the control of arrangement between atoms and molecules to form nanosystems with chemical, physical or biological properties which are different from those of molecules and bulk materials [1–3]. Metallic nanoparticles have a characteristic high surface-to-volume ratio and, consequently, a large fraction of the metal atoms at the surface, and hence are available for catalysis [4–7]. Therefore, stabilised and monodispersed palladium nanoparticles have been synthesised using sonochemical reduction processes [8–10]. It has been found that the reduction of Pd(II) ions to Pd(0) atoms is related to the intense ultrasonic waves that are strong enough to produce cavitation: formation, growth and collapse of bubbles. The reduction process and Pd<sub>n</sub>s formation can occur according to the following steps [8–10]:

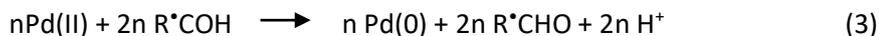
1. Pyrolyze of water into  $\cdot\text{H}$  and  $\cdot\text{OH}$  in the inner environment (gas phase) of the collapsing bubble, where elevated temperature and pressures (several thousands of degrees and hundreds of atmospheres) are proceeded.



2. Radical formation from the organic scavenger in the liquid film immediately surrounding the collapsing cavity (interfacial region with the bulk solution), where the temperature is lower than in the gas phase region



3. Reaction between the reducing radicals and the Pd(II) ions can take place in the bulk solution, which is at low temperature.



where RCH<sub>2</sub>OH: organic additive (e.g., Ethylene glycol)

It is well established that a number of parameters influence the formation process of Pd<sub>n</sub>s from Pd(0) atoms [Eq. (4)] as well as the properties of the obtained colloids. Palladium precursors [11], type of the stabiliser agent [12–15] and nature of solvent [16–18] are the important factors that control the yield and the properties of the synthesised Pd<sub>n</sub>s. There are ample reading references available on the factors that affect the preparation of Pd<sub>n</sub>s, but there is still a lack of information about the effects of ultrasonic irradiation time on the Pd<sub>n</sub>s formation mechanism. Therefore, the present experimental work was undertaken to investigate the sonochemical reduction of Pd(II) ions, Pd<sub>n</sub>s formation mechanism and to determine the role of PVP molecules at each step.

## 2. Experimental section

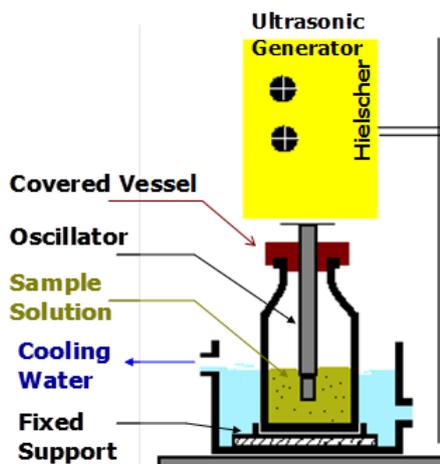


Figure 1. Schematic of experience setup used in this study

Palladium (II) nitrate solution was prepared by dissolving hydrous  $\text{Pd}(\text{NO}_3)_2$ , in dionised water. A mixture of ethylene glycol and poly (vinylpyrrolidone) was stirred under magnetic blender in a glass vessel. After this time, 1.5 mL of the solution was added to the mixture. The covered vessel was fixed, as shown in Figure 1, in the multi-wave ultrasonic generator (Hielscher), equipped with an immersed sonication horn (diameter  $\sim 12$  mm). The solution was irradiated with ultrasonic wave during several irradiation time 30, 60, 90, 120, 150 and 180 minutes.

The reduction of Pd(II) ions and the  $\text{Pd}_n\text{s}$  formation were followed by an Hitachi U-3000 UV-Visible spectrophotometer at wavelengths domain  $\lambda = 200\text{--}800$  nm. The acidity of irradiated solutions was measured by a pH meter (Crison pH 25). The role of PVP was examined by Fourier Transform Infrared spectroscopy (FTIR) using an ATI Matson Genesis series FTIR. The shape and size of the final Pd particles were determined using Transmission Electron Microscopy (TEM, Topcon 002B operating at 200 kV).

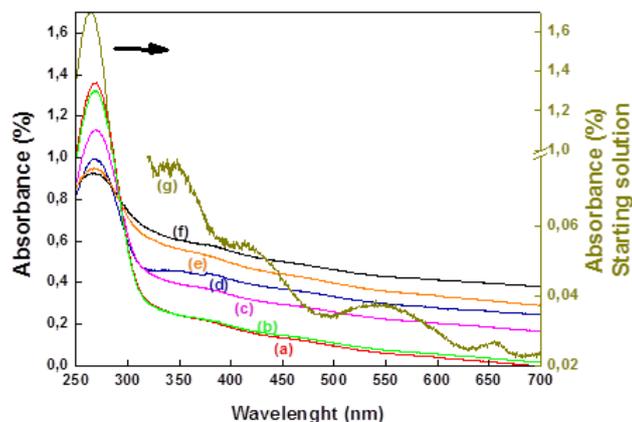


Figure 2. UV-Visible spectra of irradiated Pd colloids during (a) 30 minutes, (b) 60 minutes, (c) 90 minutes, (d) 120 minutes, (e) 150 minutes, (f) 180 minutes and (g) Starting solution. The inset gives the intensity changes of absorption peak at  $\lambda = 262$  nm

### 3. Results and discussion

#### 3.1. Kinetic of Pd(II) ions reduction

The UV-Visible absorption spectra of irradiated solutions for different ultrasound irradiation time are illustrated in Figure 2. The spectrum of starting solution [Figure 2(g)] reveals the presence of principal absorption peaks centered at 545, 415, 340 and 262 nm attributed, according to previous studies [19, 20], to the Pd(II)-complexes present in the solution. With increasing irradiation time, these absorption peaks disappeared indicating the progressive reduction of Pd(II) ions to Pd(0) atoms [21]. The decrease of the absorption peak intensity at  $\lambda = 262$  nm with increasing irradiation time, presented in the inset of Figure 2, permits to follow the reduction kinetic of Pd(II) ions [22]. One can observe that the curve has different slopes related to the changes in the Pd(II) reduction rate. For the first irradiation period, the peak intensity decreases rapidly indicating the rapid reduction of Pd(II) ions. Between 60 and 120 minutes of ultrasound irradiation, the absorption peak intensity decreases progressively. This reveals the decrease in the Pd(II) reduction rate which is probably due to the decrease of the Pd(II) concentration in the irradiated solution. Above 120 minutes of irradiation, the absorption peak intensity is relatively constant, indicating that the reduction of Pd(II) ions is very weak.

These results are confirmed by pH measurements of the obtained colloids. The variation of the acidity of Pd colloids obtained at different irradiation time is reported in Figure 3. It is well known that the change of the pH values is related to the formation of  $H^+$  ions issue from the reduction of Pd(II) ions [Eq. (4)] [23]. The pH curve can be divided into three parts: 1) up to 60 minutes of irradiation corresponding to a rapid increase of the acidity of the suspension; 2) between 60 and 120 minutes, a slight increase of the  $H^+$  concentration in the irradiated colloids; and 3) a plateau, until 180 minutes, which indicates that the reduction of Pd(II) is relatively complete.

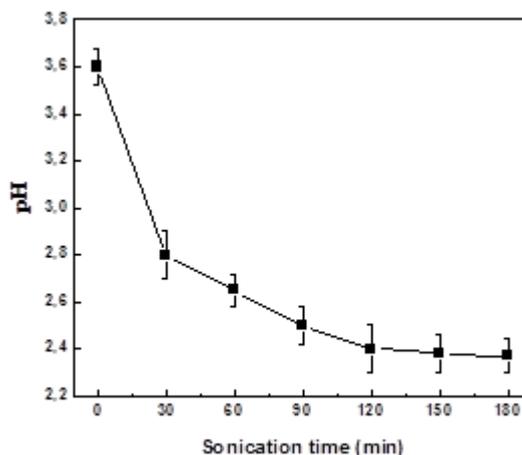


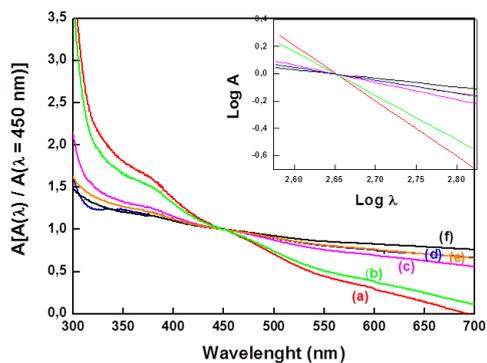
Figure 3: pH variation of Pd colloids as a function of ultrasonic irradiation time.

#### 3.2. Palladium nanoparticles formation mechanism

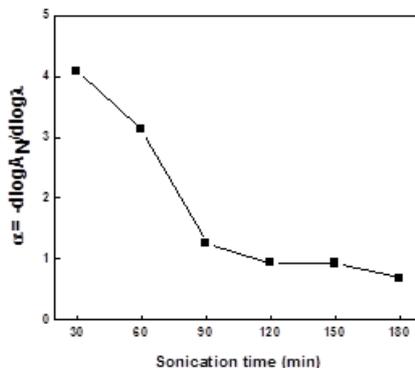
The UV-Visible spectra of irradiated Pd colloids (Figure 2) exhibit a broad continuous absorptions rise in the background towards higher energies, which are typical of those of Pd<sub>n</sub>s in the colloids [7, 19, 24]. The most striking observation in Figure 2 is the increase of the absorbance at the higher wavelengths part of all the spectra with increasing irradiation time. It is important to emphasise that at these wavelengths, the contribution to the absorbance of the starting compounds (Pd(II)-complexes) in the solutions is absent. Previous studies have proved the dependence of the UV-Visible

absorbance on the particle size. It has been reported that the absorption spectrum calculated for the particles having a diameter less than 10 nm presents a continuous increase in the absorbance with decreasing wavelength [24, 25]. Hence, the high wavelengths domain is very suitable for the study of the effect of ultrasonic irradiation time on the Pd<sub>n</sub>s size [26, 27]. Figure 4 shows the normalised absorbance ( $A_N$ ) to  $A = 1$  at  $\lambda = 450$  nm of Pd colloids in the range of 300–700 nm. The plot of  $\log A_N$  versus  $\log \lambda$ , presented in the inset, provides qualitative information about particle size. It has been demonstrated that the negative slope ( $\alpha$ ) of the double – log plot decreases with increasing particle size [28, 29]. The values of  $\alpha$ , calculated from the linear fit of log/log curves using the following formula:  $\alpha = -\frac{d\log A_N}{d\log \lambda}$ , are illustrated in Figure 5. The allure of the obtained curve indicates that

during the first 30 minutes of ultrasound irradiation ( $\alpha = 4.08$ ) the reaction leads to the formation of Pd particles with very low size. With increasing irradiation time to 60, 90 and 120 minutes, the  $\alpha$  values decrease to 3.13, 1.26 and 0.93, respectively. This indicates that the diameter of resulted particles increases progressively. Between 120 and 150 minutes, the  $\alpha$  values remain constant and close to 0.93 corresponding to a constant particle size. For the high irradiation time (180 minutes), the  $\alpha$  value presents a slight decrease to a value of about 0.63. This variation reveals that ultrasound irradiation induce a weak increase in the Pd particle size.

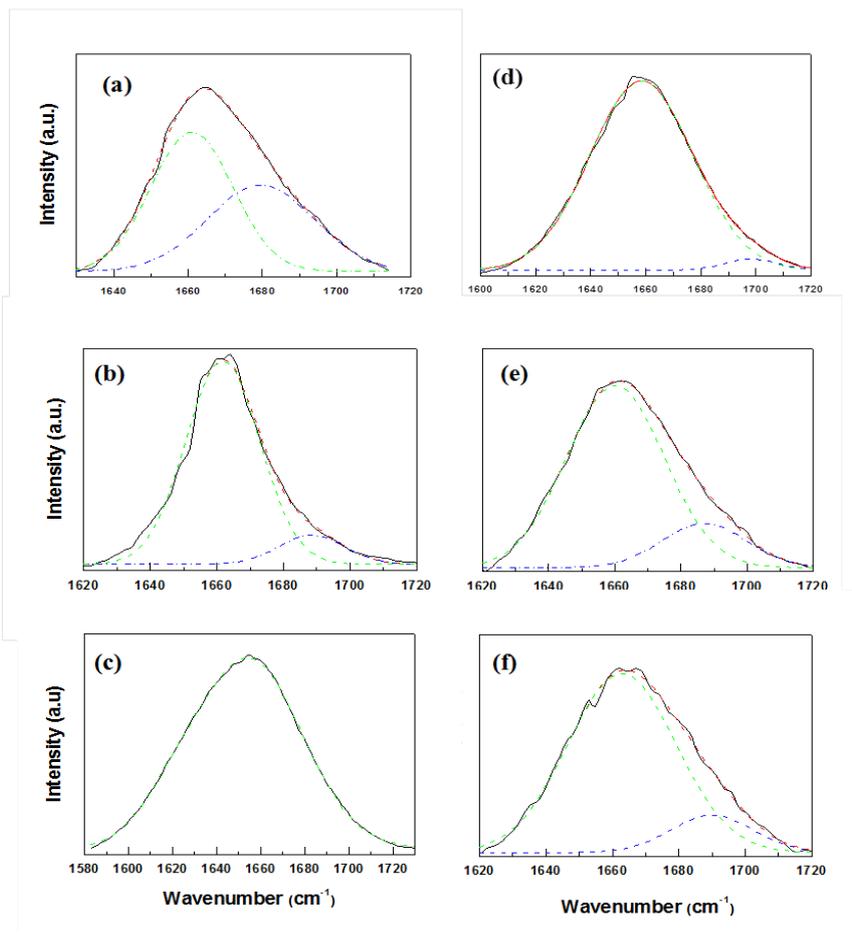


**Figure 4.** Normalised UV-Vis absorbance ( $A_N$ ) to  $A = 1$  at  $\lambda = 450$  nm of Pd colloids obtained at various irradiation time. (a) 30 minutes. (b) 60 minutes. (c) 90 minutes. (d) 120 minutes. (e) 150 minutes. (f) 180 minutes. The inset gives the UV-Vis absorption spectra on the log/log scale



**Figure 5.** Variation of  $\alpha$  as a function of irradiation time

In order to investigate the role of PVP molecules on the Pd<sub>n</sub>s colloids formation at different ultrasound irradiation time, the FTIR is a powerful tool for the characterisation of interface solid-polymer system at a molecule level [30]. It is known that the C=O (free PVP) displays a strong infrared (IR) band at around 1679 cm<sup>-1</sup> [31, 32]. In the previous study, it has been proved that the PVP molecules protect the Pd<sub>n</sub> via the coordination between the C=O (PVP) and the Pd(0) atoms on the nanoparticle surface [26]. So, the IR band of C=O (PVP) may be used as an indicator to estimate the change of the total surface of Pd<sub>n</sub>s as a function of ultrasonic irradiation time [33]. Figure 6 illustrates spectral region of C=O (PVP) band with normalised intensity in FTIR spectra of Pd<sub>n</sub>s colloids. The fit of the C=O (PVP) IR band shows that, during the first 30 minutes of irradiation, the C=O (PVP) IR position shifts towards the low frequency (1662 cm<sup>-1</sup>) indicating that PVP molecules are adsorbed on the Pd<sub>n</sub>s surface.

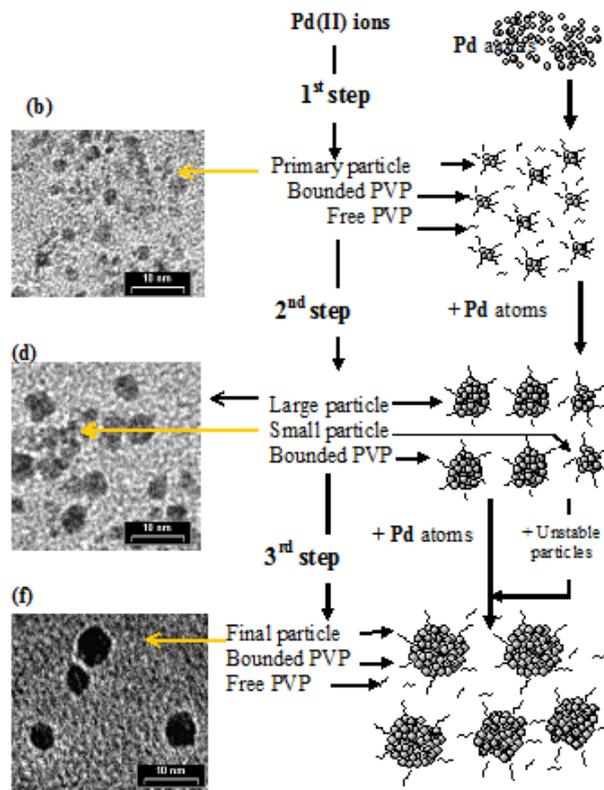


**Figure 6. Spectral regions of the C=O (PVP) bands with normalised intensity in FTIR spectra of Pd colloids measured at different irradiation time. (a) 30 minutes. (b) 60 minutes. (c) 90 minutes. (d) 120 minutes. (e) 150 minutes. (f) 180 minutes (Line: experimental data, dash: fit results).**

The presence of an IR band near 1680 cm<sup>-1</sup>, assigned to absorption of C=O (free PVP), signifies that, at this period, the available PVP molecules number is higher than the maximum PVP molecules number which can coordinate at the palladium nanoparticles surface. After 60 and 90 minutes of irradiation, the C=O (bounded PVP) IR band shifts towards the low frequency values of about 1660 and 1658 cm<sup>-1</sup>, respectively, while the C=O (free PVP) IR band intensity decreases and disappears completely after 90 minutes. These results confirm the total coordination of the PVP molecules with Pd(0) atoms at the Pd<sub>n</sub>s surface. With the increase in irradiation time (120, 150 and 180 minutes), the

C=O (bounded PVP) IR band position shifts towards the high frequencies (1660, 1662 and 1664  $\text{cm}^{-1}$ , respectively).

Simultaneously, a slight increase of the absorption intensity of C=O (free PVP) IR band is observed, which indicates that the number of free PVP molecules increase in the solution. Therefore, we suggest that the total Pd<sub>n</sub>s surface available for the coordination with the PVP molecules decreases for the long irradiation time.



**Figure 7. Expected palladium nanoparticles formation mechanism and TEM micrographs of Pd colloid irradiated at (b) 60 minutes, (d) 120 minutes and (f) 180 minutes**

According to the above results and discussions, a mechanism of PVP-Pd<sub>n</sub> formation as a function of ultrasonic irradiation time can be proposed. The mechanism, schematically depicted in Figure 7, can be divided into the following steps.

1. The first step, up to 60 minutes, corresponds to the rapid reduction of Pd(II) ions and when the concentration of saturation is reached, the formation of primary particles takes place [Figure 7(b)]. These particles are stabilised by maximal number of PVP molecules. In this step, the total PVP molecules number is greater than the PVP molecules number which can coordinate to the nuclei surface.
2. In the second step, between 60 and 120 minutes, the primary particles grow progressively by adsorption of the Pd(0) atoms depending on the rate of Pd(II) ions reduction. The obtained particles are stabilised by all available PVP molecules [Figure 7(d)].
3. In the third step, above 120 minutes, the total surface of the particles decreases (the total interaction PVP and Pd<sub>n</sub>s surface decreases). This can be explained by both the increase of the particles size ( $\alpha$  decreases slightly) and the decrease of their number. This phenomenon corresponds to the destruction of the unstable small particles under the long ultrasonic irradiation and the growth of large particles [Figure 7(f)]. Thus, at this stage, the slight growth of the stabilised

large particles is governed by the adsorption of Pd atoms on the particle surface issue from the reduction of Pd(II) ions and the destruction of unstable particles.

#### 4. Conclusions

In this study, the effects of ultrasound irradiation time on the palladium nanoparticles (Pd<sub>n</sub>s) formation mechanism and the role of the PVP at the different steps have been investigated. It was found that the rate of Pd(II) ions reduction induced by acoustic cavitation depends on the ultrasound irradiation time. The Pd<sub>n</sub>s formation mechanism suggested by UV-Visible and FTIR results is closely related to the rate of sonochemical reduction of Pd(II) ions and to the role of PVP molecules. It can be described by three important stages: 1) The formation of primary particles stabilised by maximal number of PVP molecules; 2) Progressive growth of primary particles by adsorption of the Pd(0) atoms, the obtained particles are stabilised by all available PVP molecules; 3) Stabilised large particles grow by adsorption of Pd(0) atoms resulting from both the reduction of Pd(II) ions and the destruction of unstable particles.

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