

Palladium nanoparticles synthesis using polymeric matrix: poly(ethyleneglycol) molecular weight and palladium concentration effects

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Abstract

Due to unique applications of palladium nanoparticles, synthesis of these nanoparticles by a simple and low cost method is very important. In this work, Pd nanoparticles were synthesized with narrow size distribution by loading metal salt ($\text{Pd}(\text{OAc})_2$) into the polymeric matrix (PEG) as reducing agent and stabilizer. Also, the effect of metal salt concentration and PEG molecular weight on the conversion of Pd^{2+} to nano Pd^0 and synthesized palladium nanoparticles morphology were investigated by UV-vis spectroscopy, XRD and TEM. The UV results confirmed the significant effect of PEG molecular weight on the reduction reactivity of polymeric matrix. Also, TEM and XRD results revealed that metal salt concentration has significant effect on the synthesized Pd nanoparticles size.

Keywords: Palladium; Nanoparticle; Reduction; Polymeric matrix.

1. INTRODUCTION

Nanoparticles of palladium and palladium containing intermetallic compounds (IMCs) have unique applications: sensors [1], catalysts [2] active membranes [3] and etc. Komatsu et al. [4] prepared fine particles of palladium containing intermetallic compounds (IMCs) for the oxidative acetoxylation of toluene and 1,3-butadiene (BD). Miao et al. [1] modified sensors based on the chemical modification of electrode with immobilized nanoparticles of transition metal palladium. Zhang et al. [2] synthesized nanoscale bimetallic particles (Pd/Fe, Pd/Zn, Pt/Fe, Ni/Fe) in the laboratory for treatment of chlorinated organic pollutants. Faticanti et al. [5] applied high performance nanoparticles of Pd supported on Al_2O_3 in combustion reactions. Palladium nanoparticles could be synthesized through various methods such as: sol-gel process [6], deposition via ion-exchange/adsorption [7], electrochemical method [5,8], microwave plasma

[7,9], sonochemical reduction [10] and etc. These methods suffer from a certain complexity and high cost. Therefore, using a simple method, synthesis of metal nanoparticles by loading some liquid polymeric matrices, will be appropriate. Huang et al. [11] synthesized phenanthroline-stabilized palladium nanoparticles dispersed in ionic liquid. However, ionic liquid is not only very expensive but also not yet accepted as an environmentally friendly medium [12-13]. Therefore, it is desirable to develop an alternative environmentally friendly medium in place of the volatile and toxic organic solvents. Pillai et al. [12] synthesized palladium nanoparticles in PEG by using phenanthroline as stabilizer under an atmosphere of hydrogen. But, using of a controlled atmosphere with stabilizer cause to undesirable increase in complexity and cost of the introduced synthesis method. Therefore, development of this method with simple and facile conditions will be important and desirable in synthesis of metal (palladium) nanoparticles.

Table 1: Characteristics of materials

Materials	Function	Molecular formula	Characteristics	Supplier
Solid Brown Powder				
Palladium acetate	Palladium Precursor	$C_4H_6O_4Pd$	Mw: 224.49	Merck ¹
Ave. Molecular Weight:				
Poly(ethyleneglycole)	Reducing agent	$HO(C_2H_4O)_nH$	2000, 6000 and 35000	Merck ¹
Methane Dichloride	Solvent	CH_2Cl_2	Transparent Liquid	Merck ¹

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In this study, unlike the previous work results [12], palladium nanoparticles with narrow size distribution via a simple and facile route were synthesized by exploiting PEG as both reducing agent and stabilizer. Also, the molecular weight of polymeric matrix (PEG) and palladium concentration effects on the conversion of Pd^{2+} to nano Pd^0 and synthesized palladium nanoparticles morphology were investigated by UV-vis spectroscopy, X-ray diffraction (XRD) and Transmission Electron Microscopy (TEM) methods.

2. EXPERIMENTAL

2.1. Materials

The characteristics of the materials used in this work are given in Table 1.

2.2. Preparation of nano-Pd

Palladium acetate was added into the polymeric matrix at temperature above the melting point of PEG by magnetic stirring. The resulting light yellow homogeneous solution was further stirred for 2 hours at the same temperature. During this process the color of the solution changed from light yellow to brown and finally turned black, indicating the formation of Pd metal. The process then followed by ultrasonic irradiation of solution for 1 hour at the same temperature. Then the mixture of PEG and palladium nanoparticles was cooled immediately to ambient temperature to form a solidified mixture.

2.3. Characterization

UV-vis spectroscopy measurements (325–900 nm) were performed on a Spectronic 401 – MILTON ROY. 0.55 mM palladium solutions in CH_2Cl_2 prepared for UV-vis measurements. The XRD patterns of Pd nanoparticles were determined on a TW3710 Philips X'Pert diffractometer using $CuK\alpha$ as radiation and $CuK\alpha$ as a filter ($\lambda=1.54 \text{ \AA}$). Data were collected in the range $5 \leq 2\theta \leq 80$ with a 0.02° 2θ -step and 2 sec per step (40 kV and 30 mA). The average size of crystallites was calculated from the peak broad (111) by using the Debye–Scherrer equation [8]. The transmission electron micrographs were obtained by employing CM-200 FEG Philips microscope. TEM samples were prepared by solving Pd/PEG in CH_2Cl_2 and then drops of prepared colloidal solution were placed onto a carbon-coated copper grid.

3. RESULTS AND DISCUSSION

3.1. Reduction of Palladium

The mixtures of PEG and Pd nanoparticles were prepared through adding various amounts of palladium acetate into 4 gr PEG with different molecular weights (2000, 6000 and 35000).

Figure 1a displayed the UV-vis spectra of palladium acetate. As can be seen, the UV-vis spectra of $Pd(OAc)_2$ reveal a peak at 400 nm refer to the existence of Pd(II) [14].

Figure 1b showed the result of UV-vis spectra of palladium nanoparticles by using PEG 2000

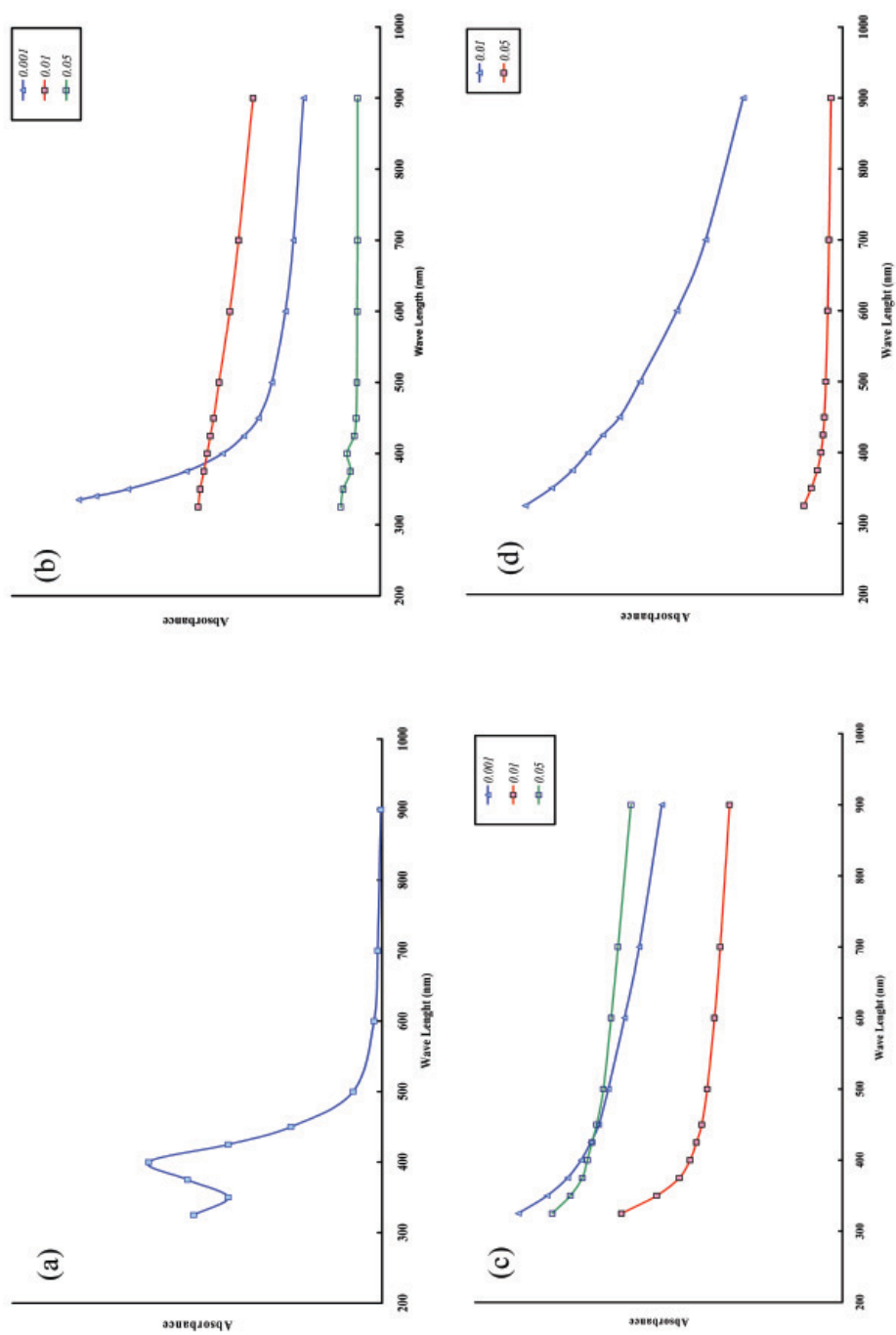


Figure 1: UV-vis spectra of (a) Pd(OAc)₂, (b) PEG 2000, (c) PEG 6000 and (d) PEG 35000 at different palladium acetate concentration (gr Pd(OAc)₂ per 4 gr PEG)

as reducing agent. By using PEG 2000 the peak at 400 nm entirely removed for low $\text{Pd}(\text{OAc})_2$ concentrations, indicating complete reduction of $\text{Pd}(\text{II})$ to Pd nanoparticles. A weak absorbance intensity using 0.05 gr of $\text{Pd}(\text{OAc})_2$ was observed at 400 nm, shows that palladium nanoparticles were developed at low concentrations. Hence the reduction strength of PEG 2000 is not high enough to reduce entire $\text{Pd}(\text{OAc})_2$ in high concentrations. Figure 1c presented the results of UV-vis spectra of palladium nanoparticles by using PEG 6000. In the cases of using PEG 6000, the peak at 400 nm was disappeared completely for all $\text{Pd}(\text{OAc})_2$ concentrations, reveal that full conversion of $\text{Pd}(\text{II})$ to nano-Pd. Also the same behavior was shown in Figure 1d for PEG 35000.

Figure 2 displayed the UV-vis spectra of the palladium nanoparticles were produced through reduction of 0.05 gr $\text{Pd}(\text{OAc})_2$ by using different molecular weight PEG as reducing agent.

A weak absorbance intensity using PEG 2000 was observed at 400 nm, showing that palladium nanoparticles were developed at low concentrations. In the cases of using PEG 6000, the peak at 400 nm was disappeared, reveal that full conversion of $\text{Pd}(\text{II})$ to nano-Pd. Further increasing of PEG molecular weight results in the rapid reduction of

$\text{Pd}(\text{II})$ to Pd nanoparticles, which can be due to the high reducing reactivity of high molecular weight PEG. Therefore, because of partial reduction in the cases of using PEG 2000 and high viscosity of PEG 35000, PEG 6000 selected for more analysis.

3.2. Crystal structure

The crystalline properties of the prepared samples were investigated by X-ray Diffraction (XRD). The result of typical XRD pattern was shown in Figure 3. The two prominent peaks of PEG (at $2\theta = 19.2$ and 23.4°) were presented in this pattern, indicating the presence of pure polymer, also the characteristic peak of Pd (about $2\theta = 40$) was presented [15]. Also, the XRD patterns of samples were prepared by using PEG 6000 are shown in the inset of Figure 3. As can be seen, the intensity of palladium peaks increases at high $\text{Pd}(\text{OAc})_2$ concentrations. The obtained cluster size of palladium nanoparticles using the Scherrer formula showed that the synthesized nanoparticles size are increased significantly by increasing palladium acetate concentration.

3.3. Particle size and morphology

Transmission electron microscope (TEM) analysis visualized the presence of narrow size distributed palladium nanoparticles. Figure 4 presents the

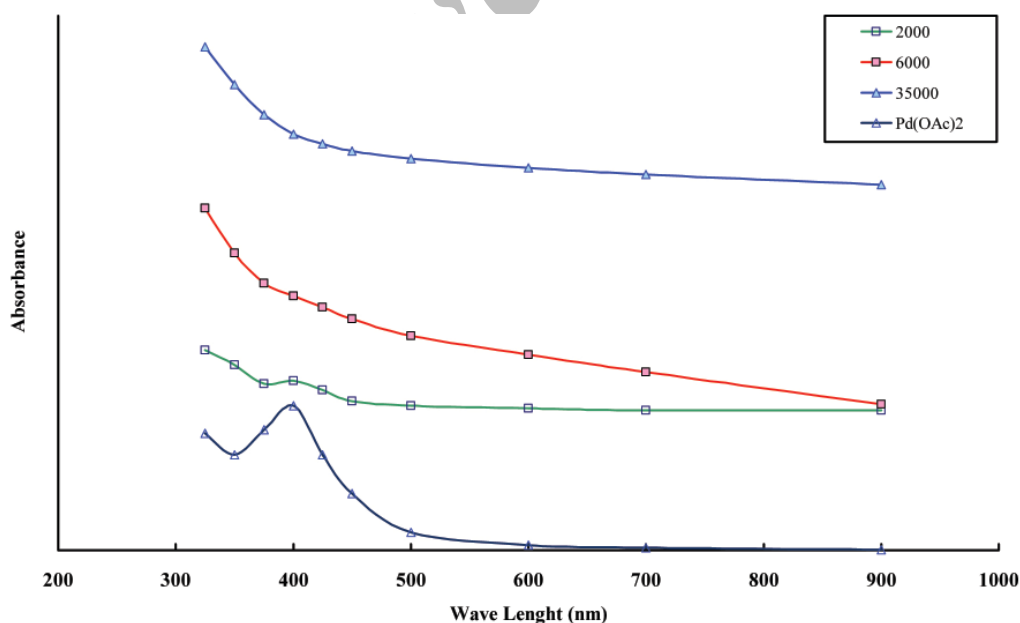


Figure 2: UV-vis spectra of palladium nanoparticles were prepared by different PEG molecular weights.

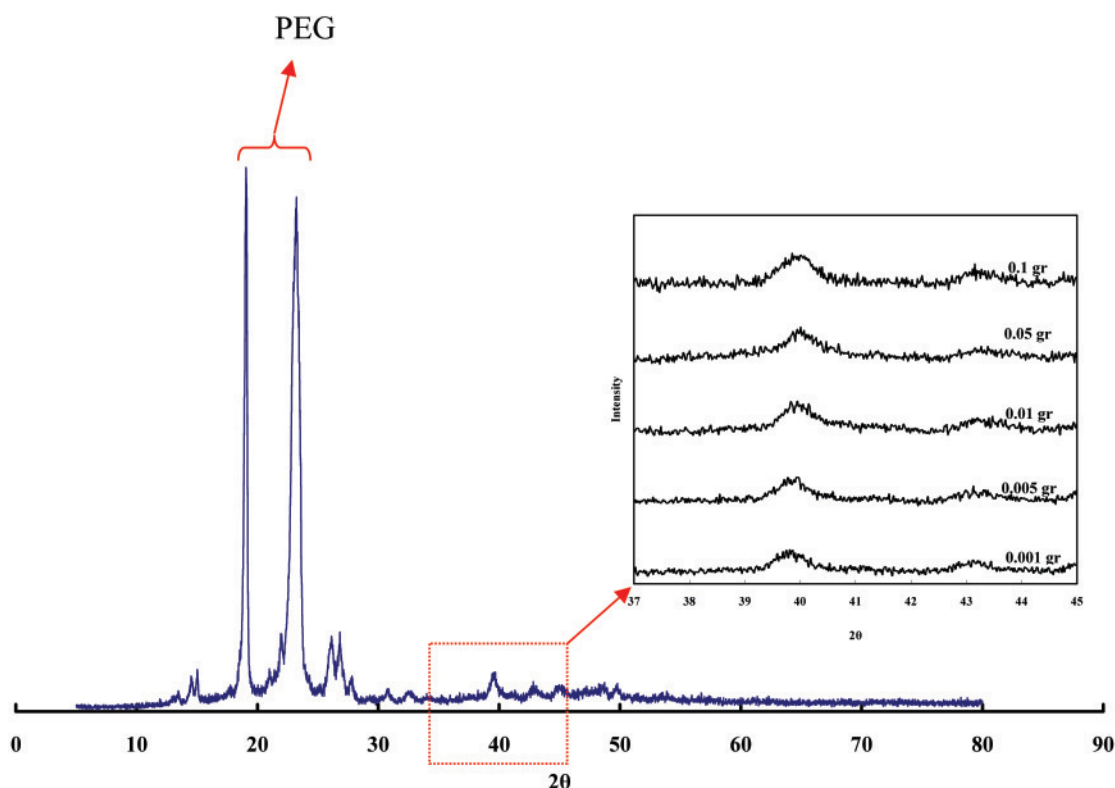


Figure 3: XRD pattern of the synthesized Pd nanoparticles in PEG matrix. The inset is related to different amounts of Pd(OAc)₂ in PEG 6000.

TEM images of palladium nanoparticles prepared by adding different amounts of Pd(OAc)₂ into 4 gr PEG 6000.

At very low concentrations, palladium nanoparticles are not clearly detectable in the polymeric matrix. By increasing Pd(OAc)₂ concentration, Pd nanoparticles could be observable, so that in the case of using 0.01 gr Pd(OAc)₂, spherical Pd nanoparticles with the average dimensions less than 5 nm are obviously visible in the polymeric matrix. Also TEM images of sample were prepared by using 0.05 Pd(OAc)₂ exhibit palladium nanoparticles with greater dimensions (5 nm). It seems that the concentration increasing affects on the particle size significantly which is in good agreement with XRD results.

4. CONCLUSION

In this study, unlike the previous work results [12], palladium nanoparticles with narrow size distribution were synthesized by loading metal salt into the PEG matrix as reducing agent and stabilizer. The results of UV show that the PEG molecular weight has significant effect on reducing reactivity of polymeric matrix and at high metal salt concentration, the reduction of Pd(II) can not be occurred completely by low molecular weight polymers. Also, both XRD and TEM results reveal that the metal salt concentration has significant effect on the synthesized Pd nanoparticles size.

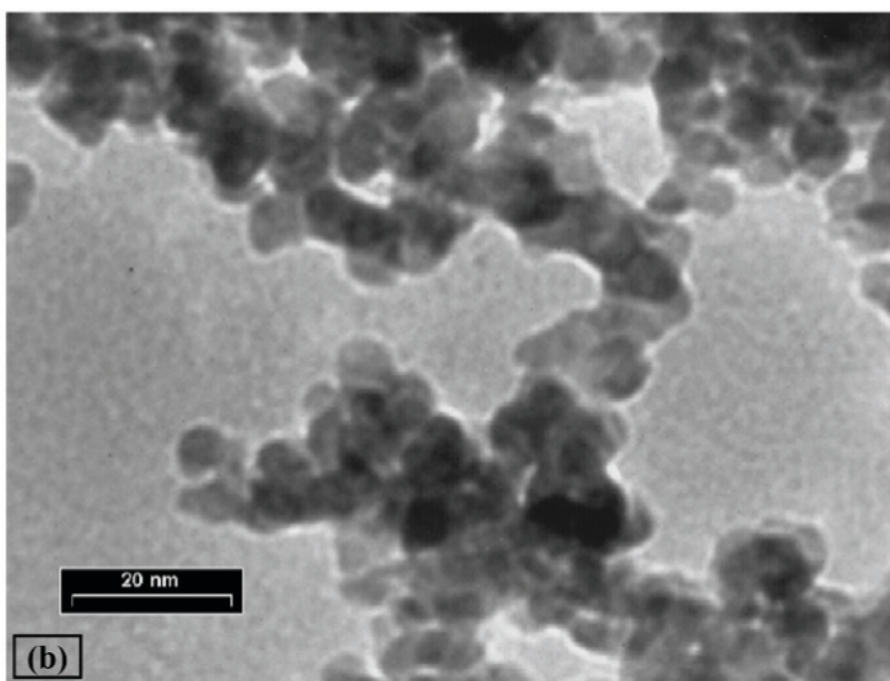
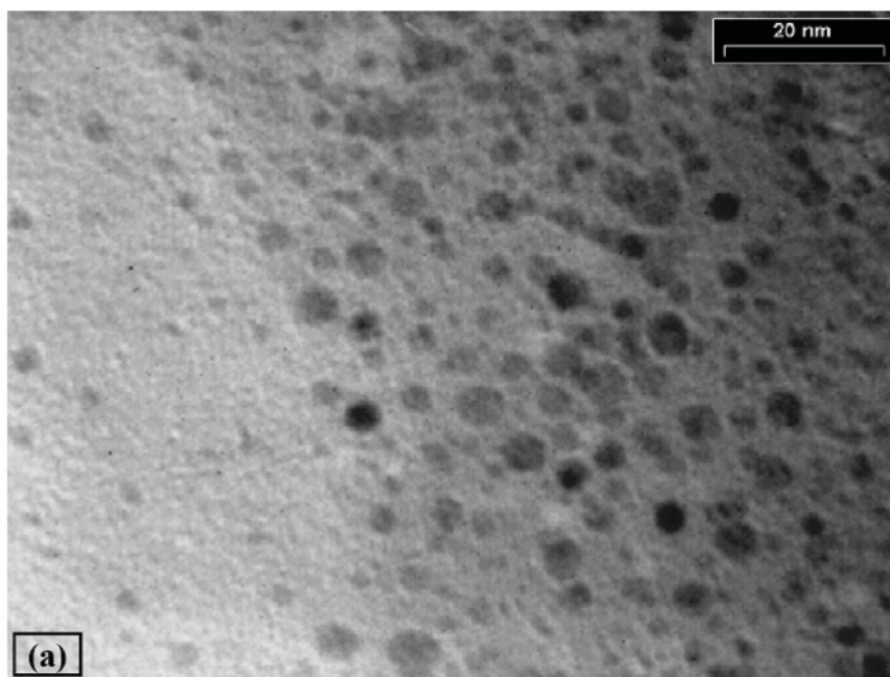


Figure 4: TEM images of Pd nanoparticles were prepared at different amounts of Pd(OAc)₂:
(a) 0.01 and (b) 0.05 gr Pd(OAc)₂ per 4 gr PEG 6000

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