VNU Journal of Science: Mathematics – Physics, Vol. 30, No. 2 (2014) 18-24

Preparation of Platinum Nanoparticles in Solution of Polyvinyl Pyrrolydone (PVP) by Laser Ablation Method

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Received 25 April 2014
Revised 20 May 2014; Accepted 18 June 2014

Abstract: Using Nd:YAG laser we studied to produce platinum nanoparticles (PtNPs) in solution of polyvinyl pyrrolidone $(C_6H_9NO)_n$ (PVP) by laser ablation method. The influence of average laser power, laser irradiation time, laser wave length and concentration of PVP solution in water on morphology, size distribution of PtNPs was investigated. The mean diameter of the PtNPs in 0.01M PVP solution was of 9 nm. The results on an optimum laser ablation process for preparation of PtNPs in PVP solution were discussed in this paper.

Keywords: Laser ablation, plasmon resonance, nanoparticle, second harmonic.

1. Introduction

Noble metal nanoparticles in liquid have become a promising material for variety of applications such as nonlinear optical devices, optical recording media, biosensing and bioimaging applications [1-3]. Several chemical and physical or electrochemical methods have been developed to produce metal nanoparticles such as chemical reduction [4], gamma irradiation [5], electron irradiation [6], photochemical method [7], microwave processing [8] and sonoelectrochemical method [9]. In recent years, pulsed laser ablation method was employed for preparation of several metal and semiconductor materials in different media. One of the advantages of laser ablation method in comparison with other conventional methods is the possible easy synthesis of nanoparticles in arbitrary liquids including organic liquids and biological-friendly environments without contamination by reducing agents [10]. Recently, we develop laser ablation method and successfully produced Au, Ag and Cu nanoparticles in different solutions and pure liquids [11-12]

In this work, we prepared PtNP in PVP $(C_6H_9NO)_n$ solution by using laser ablation method. Factors including laser irradiation time, laser wavelength and PVP concentration that affect morphology, size distribution of PtNPs were investigated to find out an optimal ablation procedure. The results of the investigation are also discussed and presented.

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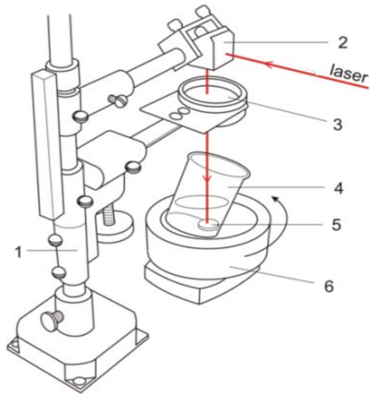
2. Experimental

The experimental set-up of laser ablation is shown in Fig 1. Laser beam from a Nd: YAG laser (Quanta Ray Pro 230-USA) was focused on a platinum plate (99.9% in purity) placed in a glass vessel filed with 10 ml of PVP solution by a lens having focal length of 150 mm. The laser was set in Q-switch mode to give laser pulse duration of 8 ns, repetition rate of 10Hz.



(a)

(b)

Fig.1. Experiment set-up (a) and picture of Nd:YAG laser (b)
1. Holder 2. Prism 3. Lens 4. Glass vessel 5. Pt plate 6. Rotary system

The PVP solution vessel was placed on a support which executed repetitive circular motions at a constant speed to prevent agglomeration of particles. PVP solutions in distilled water were prepared in different concentrations. The solution becomes colored under action of the laser beam. A small amount of the colored solution was extracted for absorption measurement and TEM observation. The absorption spectrum was measured on a Shimadzu UV-Vis 2450 spectrometer. The TEM micrograph was done on a JEM 1010-JEOL. The size of nanoparticles was determined by ImagieJ 1.37V software of Wayne Rasband (National institutes of Health, USA). The size distribution was obtained by measuring the diameter of more than 500 particles and using Origin 7.5 software. PVP solutions in distilled water were prepared in mol concentrations of 0.005 M, 0.010 M, 0.015 M and 0.020 M. The PVP solutions play the role of the surfactant in the preparation of PtNPs [13]. The ablation of Pt plate can be carry out by the 1064 nm fundamental wavelength, 532nm second harmonic or 355 nm third harmonic of Nd:YAG laser.

3. Results and discussion

Using 532 nm wavelength of Nd:YAG laser with average power of 400mW, irradiation time of 15 min, PtNPs in PVP solution with concentrations of 0.010 M . XRD patterns of the PtNPs are shown in Fig.2.

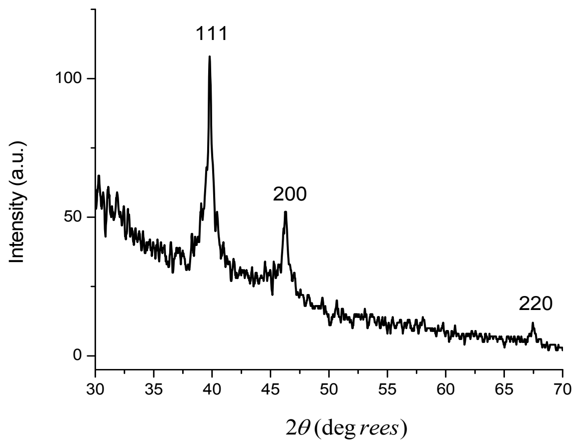


Fig.2. XRD patterns of the Pt NPs produced in PVP solution.

In the XRD patterns there are 3 peaks at 2θ $=39.8^o, 46.3^o$ and 67.4^o. These peaks correspond to the characteristic diffraction peaks of the FCC crystalline structure of Pt. The (111) peak is the strongest. The UV-Vis absorption spectra of Pt nanoparticle colloids produced in PVP solution are shown in Fig.3. The characteristic plasmon resonance absorption peak of Pt nanoparticle colloids was observed at 233 nm.

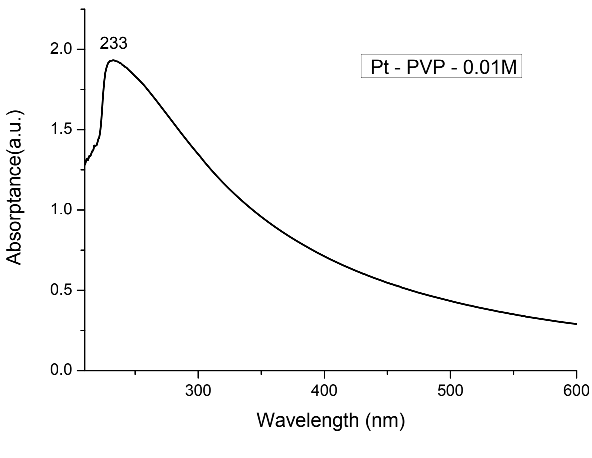
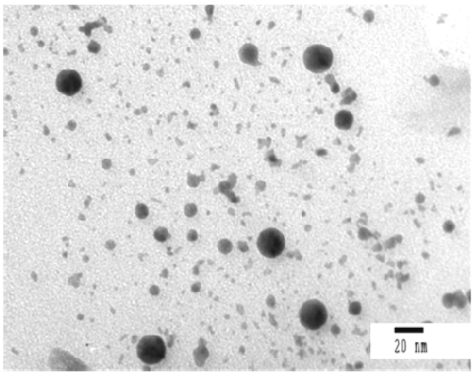
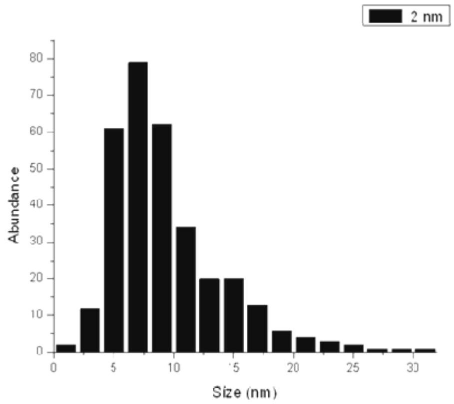


Fig. 3. UV-Vis absorption spectrum of Pt PNs produced in PVP solutions of 0.01M.

Fig.4 shows a TEM image and the size distribution of the PtNPs produced in 0.01M PVP solution using 532nm wavelength with an average laser power of 400mW and laser irradiation time of 15 min. From this figure it is seen that the diameter of Pt nanoparticles ranges from 2 to 20 nm. The average size of Pt nanoparticles is 9 nm





(a) (b)

Fig.4. TEM image (a) and size distribution (b) of the Pt NPs produced in 0.01M PVP solution.

To study the role of laser influence and laser irradiation time in the ablation procedure we have prepared PtNPs with different average laser powers and laser irradiation times. The absorption spectra of PtNPs prepared in 0.01M PVP solution using 1064 nm wavelength with different average laser powers ranging from 200mW to 550mW and laser irradiation time of 15 minutes are plotted in Fig.5.

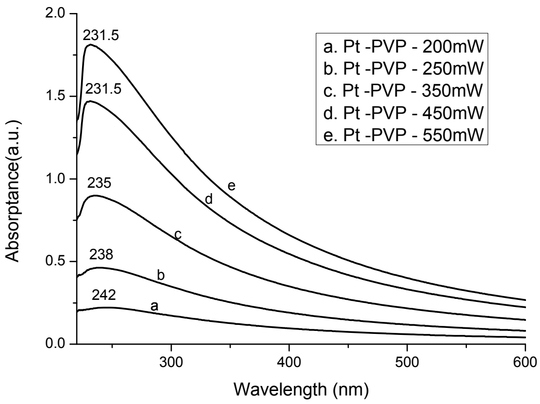


Fig.5. UV-Vis absorption spectra of Pt NPs prepared by different average laser powers,

From Fig. 5, one can see that with the increase of the average laser power, from 200 mW to 550 mW, the absorptance increases and the absorption peak is shifted to the shorter wavelength (blue shift). According to the Mie theory for sphere nanoparticles [14-17], the blue shift of the resonance plasmon absorption peak proves the decrease of the nanoparticle size.

Fig.6 shows UV-Vis absorption spectra of PtNPs produced in 0.01M PVP solution by 400 mW average laser power with different laser exposure time.

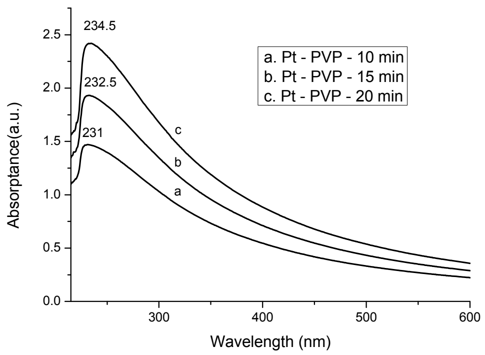


Fig.6. UV-Vis absorption spectra of Pt NPs prepared with different laser exposure times.

As seen from Fig.6, the abundance of Pt PNs increases and the absorption peak is shifted to longer wavelength (red shift) with the increase of laser exposure time from 10 to 20 min. Using 1064 nm fundamental wavelength and 532nm, 355nm harmonics of Nd:YAG laser, we investigated the influence of different laser wavelengths in the process. The absorption spectra of Pt NPs prepared in 0.01 PVP solution by average laser power of 250mW with different laser wavelengths are shown in Fig.7.

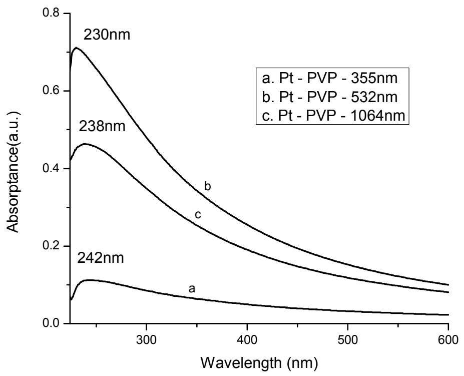


Fig.7. UV-Vis absorption spectra of Pt NPs prepared by different laser wavelengths, average laser power of 250mW, laser exposure time of 10 min.

The obtained result in Fig.7 shows that the absorption peak corresponding to the wavelength of 532 nm is highest, meanwhile the one corresponding to the wavelength of 355 nm is lowest. This means that the laser ablation efficiency is lowest at the laser wavelength of 355 nm in the experimental conditions. It is contrast to the case of ablation in air where the shorter wavelength (355 nm) or higher photon energy ablates metal more strongly than the longer wavelength (1064 nm). The low laser ablation efficiency can be explained by the absorption effect of PtNP colloid on laser beam of 355 nm wavelength which is near the resonance Plasmon absorption peak of Pt NPs. Meanwhile, the 1064nm and 532nm wavelengths are far from the resonance absorption peak (Fig. 7) and the shorter wavelength (532nm) with higher photon energy ablates metal more strongly than the longer wavelength (1064 nm). The 532 nm wavelength gives highest laser ablation efficiency in these experimental conditions.

The influence of PVP concentration on PtNPs size was also investigated. Fig. 8 presents the absorption spectra of PtNPs prepared in different concentrations of PVP solution by average laser power of 300mW, laser exposure time of 15 minutes.

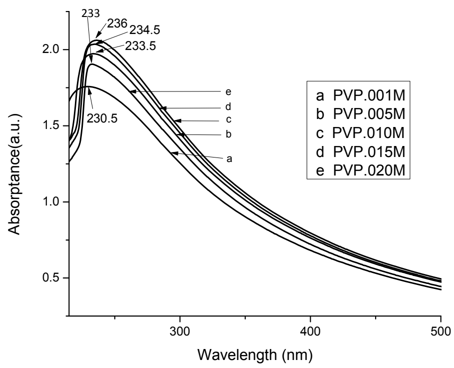


Fig. 8. The UV-Vis absorption spectra of Pt NPs prepared in different concentrations of PVP solution by 1064nm wavelengths, average laser power of 400mW, laser exposure time of 15 min.

With the increase of the PVP concentration, from 0.001M to 0.01M, the absorption profiles become narrower and the characteristic plasmon resonance absorption peaks of PtNPs are shifted from 230.5 nm to 236 nm. When the PVP concentration increases from 0.001M to 0.01M, the plasmon resonance absorption peak is shifted from 230.5 to 236nm (red shift). When the PVP concentration increases from 0.01M to 0.02M, the plasmon resonance absorption peak is shifted from 236 nm to 233 nm respectively (blue shift).

The fact that the absorption spectrum profile is narrower proves that the decrease of the dispersion of size distribution can be explained by the presence of PVP. Indeed, in the presence of PVP - $(C_6H_9NO)_n$, the C=O group of the polymer interacts with metal atoms on the surface of nanoparticles. The oxygen atoms of C=O group are attached to the metal atoms and create local surface state that protect metal nanoparticles against growth and aggregation [18].

4. Conclusion

With the aim to find out an optimum laser ablation process for preparation of PtNPs in PVP solution, the affect of laser power, laser wavelength, laser exposure time and concentration of PVP on morphology, size distribution and optical properties of Pt NPs was investigated. Among 3 wavelengths of Nd:YAG laser used (namely 355, 532 and 1064 nm), the 532nm wavelength gave the highest laser ablation efficiency. The role of PVP solution as a surfactant for Pt NPs was elucidated. With increase of the PVP concentration, from 0.001M to 0.02M, the UV-Vis absorption spectrum profiles become narrower and characteristic plasmon resonance absorption peak of PtNPs is shifted. The obtained results showed that the size of PtNPs can be controlled by changing PVP concentration and laser parameters.

Acknowledgments

This research was supported by the Project QGTĐ.12.01, VNU Hanoi.

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