Preparation of platinum nanoparticles in liquids by laser ablation method

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Abstract

Platinum (Pt) nanoparticles were prepared in solutions of ethanol and TSC (trisodium citrate—Na$_3$C$_6$H$_5$O$_7.n$H$_2$O) in water by laser ablation method using Nd:YAG laser. The role of laser fluence, laser wavelength and concentration of surfactant liquids in laser ablation process were investigated. The morphology, size distribution and optical properties of the Pt nanoparticles (NPs) were observed by transmission electron microscopy (TEM), UV-vis spectrometer and x-ray diffraction measurements. The average diameter of Pt NPs prepared in ethanol and TSC solutions ranges around 7–9 nm and 10–12 nm, respectively. The results showed advantages of the laser ablation method.

Keywords: nanoparticle, surfactant, laser ablation, plasmon resonance absorption

1. Introduction

Colloidal noble metal nanoparticles are of great interest because of their size dependent optical properties, magnetic properties and catalytic activities. Noble metal nanoparticles in liquid environment have become a promising material for a variety of applications such as nonlinear optical devices, optical recording media, biosensing and bioimaging applications. Among noble metal nanoparticles, platinum and its alloy nanoparticles have attracted much attention because they are excellent catalysts for many purposes [1–5].

Many techniques have been developed to prepare metal nanoparticles such as chemical reduction, electrochemical reduction, radiolytic reduction, laser ablation.

Laser ablation in liquids is promising as a rapid, simple and most versatile technique to prepare noble metal nanoparticles for analytical chemical and biological sensing applications. Metal nanoparticles could be prepared by laser ablation in clean liquids without contamination.

Surface contamination during laser ablation is greatly reduced compared to the standard chemical synthesis involving reduction of metal salts because the particles are formed directly from ablation of a pure target in a pure solvent [6–8]. In addition, laser ablation provides a technique to control size of nanoparticles by changing the nature of liquid carrier medium [9].

We have previously reported our investigations on the formation of silver and gold nanoparticles by laser ablation in several liquids [10, 11]. In this paper, we report our investigations of Pt NPs preparation in clean and biologically-friendly liquids such as pure water, ethanol and TSC solution in water by laser ablation.

2. Experimental

Platinum nanoparticles were prepared by laser ablation of a platinum plate (99.9% in purity) in 10 ml liquid. The liquid is a solution of TSC or ethanol in water with different concentrations. A Nd:YAG laser (Quanta Ray Pro 230-USA) was set in Q-switching mode to give laser pulses of 8 ns duration with repetition rate of 10 Hz. The laser beam with different wavelengths (1064 nm, 532 nm and 355 nm) was focused on the Pt plate by a lens having the focal length of 150 mm. The liquid vessel was placed on a horizontal platform, which executed repetitive circular motions at a constant speed to prevent agglomeration of particles. The solution became colored under action of the laser beam. A small amount of the colored solution was extracted for absorption measurements.
and TEM observation. The absorption spectrum was measured by a Shimadzu UV-vis 2450 spectrometer. The TEM micrograph was taken by a JEM 1010-JEOL. The size of nanoparticles was determined by ImageJ 1.37V software from 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.

3. Results and discussion

3.1. Preparation of Pt nanoparticles in TSC solution

We chose TSC (trisodium citrate-Na₃C₆H₅O₇.nH₂O) solution in water because it is a non-toxic and biocompatible solution. The TSC solution in distilled water was prepared with different concentrations.

The morphology and size of metal nanoparticles depend on many factors such as laser fluence, laser irradiation time, laser wavelength and concentration of surfactant solution in laser ablation process. We considered all these factors to get a suitable laser ablation procedure. Using 1064 nm wavelength of Nd:YAG laser with average power of 450 mW, irradiation time of 15 min we prepared Pt NPs in TSC solution with concentrations of 0.1 g L⁻¹, 0.5 g L⁻¹ and 1 g L⁻¹.

The TEM images of colloidal Pt NPs were presented in figure 1. The TEM images show that the Pt NPs are rather spherical in shape. The data of size and size distribution of Pt NPs were analyzed and are given in figure 2. Analysis from size distribution shows the mean diameters of Pt NPs prepared in TSC solutions of 0.1 g L⁻¹, 0.5 g L⁻¹ and 1 g L⁻¹ are 7 nm, 8 nm and 9 nm, respectively.

The UV-vis absorption spectra of Pt nanoparticle colloids prepared in TSC solutions are shown in figure 3. The characteristic plasmon resonance absorption peaks of Pt nanoparticle colloids prepared in 0.1 g L⁻¹, 0.5 g L⁻¹ and 1 g L⁻¹ TSC solutions are 226 nm, 247 nm and 266 nm, respectively. The results show that mean size of Pt NPs changes clearly when TSC concentration increases from 0.1 g L⁻¹ to 1 g L⁻¹.

The x-ray diffraction (XRD) pattern of the Pt NPs show in figure 4 three peaks at 2θ = 39.8°, 46.3° and 67.4° corresponding to the characteristic diffraction peaks of face centered cubic (fcc) lattice of Pt.

We repeated the laser ablation procedure with 532 nm and 355 nm wavelength of Nd:YAG laser. Figure 5 shows absorption spectra of colloidal Pt NPs prepared in 5 g L⁻¹ TSC solution by 1064 nm, 532 nm and 355 nm wavelengths with average laser power of 450 mW.

The results in figure 5 show that the absorption peak corresponding to the wavelength of 1064 nm is highest, meanwhile the one corresponding to the wavelength of 355 nm is lowest. That means the laser ablation efficiency is lowest at the laser wavelength of 355 nm in this experimental condition. The low laser ablation efficiency can be explained by the absorption effect of Pt NP colloid on laser beam of 355 nm wavelength which is near the resonance plasmon absorption peak of Pt NPs.
3.2. Preparation of Pt NPs in ethanol solution

By the same method we prepared Pt NPs in ethanol solution. Figure 6 shows TEM image, size distribution and XRD spectrum of the Pt NPs prepared in 40% ethanol solution in water using 1064 nm wavelength with the average laser power of 500 mW and laser irradiation time of 15 min. The results show that the diameter of Pt NPs ranges from 2 nm to 20 nm and the mean diameter of Pt NPs is 9 nm. The XRD pattern showed the same peaks as Pt NPs prepared in TSC solution (three peaks at $2\theta = 39.8^\circ$, 46.3° and 67.4°).

The laser ablation of platinum was carried out by different laser powers with the same irradiation time of 15 min and wavelength of 1064 nm. The UV-vis absorption spectra of Pt NP colloids prepared by average laser powers of 400 mW, 500 mW and 600 mW are presented in figure 7.

As seen in figure 7 the position of absorption peak is almost unchanged when the average laser power increases.
from 400 mW to 600 mW. The increase of laser power affects unnoticeably the size of Pt nanoparticles prepared in ethanol solution. Meanwhile, the laser ablation efficiency increases when average laser powers increases from 400 mW to 500 mW and then remains unchanged when average laser power increases from 500 mW to 600 mW.

Using average laser powers of 500 mW we considered the laser ablation of Pt plate in pure water and ethanol solutions in water of different concentrations (20%, 40%, 60%, 80%). The UV-vis absorption spectra of the colloidal Pt NPs are given in figure 8.

4. Conclusion
Pt NPs were prepared in TSC and ethanol solutions in water by laser ablation method. The influence of laser fluence, laser power and laser efficiency on the size of Pt NPs are investigated. The absorption spectra of Pt NP colloids produced by average laser powers of (a) 400 mW, (b) 500 mW and (c) 600 mW are shown in figure 7. The position of characteristic plasmon resonance absorption peaks of colloidal Pt NPs is shifted from 260 nm to 272 nm when the ethanol concentration increases from 0 to 80%. According to Mie’s theory, that means the size of Pt NPs increases when the ethanol concentration increases [12–14].
wavelength and concentration of surfactant liquids on morphology, size distribution and optical properties of Pt NPs were investigated to get a suitable laser ablation procedure. The mean size of Pt NPs changed clearly when using different concentrations of TSC and ethanol in water. This result supports a size control method in preparation of Pt NPs by laser ablation.

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Figure 8. The absorption spectra of Pt NPs in water (a) and in different concentrations of ethanol solutions of 20% (b), 40% (c), 60% (d) and 80% (e).