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Preparation of copper nanoparticles in water and acetone by laser ablation

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Abstract. Using the Quanta Ray Pro 230 Nd:YAG laser, we produced copper nanoparticles in water and acetone by laser ablation. The average size and optical properties of the nanoparticles were observed by a transmission electron microscopy (JEM 1010 – JEOL) and UV–visible 2450 spectrometer. The average diameter of copper nanoparticles in water and acetone were 23 nm and 5 nm, respectively. The absorption spectra of copper nanoparticles showed that there was no indication of copper oxide nanoparticles. The experimental results showed advantages of the laser ablation method. The results and discussions will be represented in this report.

Keywords: laser ablation, plasmon resonance, nanoparticles

1. Introduction

Metal nanoparticles are very attractive due to their unique physical and chemical properties. They have a wide range of optical and electrical properties that originate from quantum confinement effects. In recent years, copper nanoparticles have attracted great interest due to their potential applications in conductive films, lubrication, nanofluids and catalysis. Besides bulk materials, nanoparticles are efficient for catalysis applications because of their large surface to volume ratio. In addition, copper nanoparticles embedded in a dielectric medium such as polymer matrices are useful materials for nonlinear optical devices [1,2]. A number of methods, including microemulsion, reverse micelles and reduction of copper salts have been developed to prepare copper nanoparticles [3]. Recently, the use of pulsed laser ablation of materials for preparation of silver and gold nanopareticles has been studied in our Quant um Optics Lab. In this paper, we report the preparation of copper nanoparticles by laser ablation in distilled water and pure aceton. The copper nanoparticles were produced with different laser powers. The average size and size distribution of copper nanoparticles were observed to determine the optimal laser ablation process.

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2. Experimental

Experimental setup was shown in Fig 1.

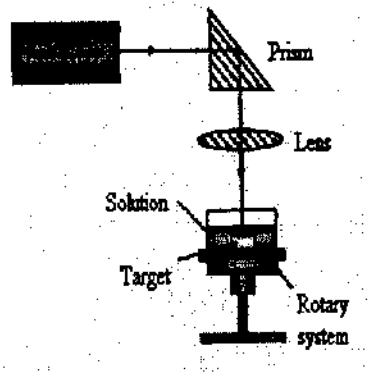

Fig. 1. Experimental setup.

We placed a copper plate (99,9% in purity) in a glass cuvette filed with 10ml aqueous solution of surfactant. The fundamental wavelength (1064 nm) of the Quanta Ray Pro 230 Nd: YAG laser was focused on the copper plate by a lens having the focal length of 150mm. The laser was set in Q-switch mode to give laser pulse duration of 8 ns, repetition rate of 10Hz.

Copper nanoparticles were produced by laser ablation of copper plate immersed in water and acetone. The vessel was placed on a horizontal platform, which executed repetitive circular motions at a constant speed to prevent agglomeration of particles. 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 by a Shimadzu UV-2450 spectrometer. The TEM micrograph was taken by 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.

3. Results and discussion

First, we studied to prepare copper nanoparticles in distilled water. The ablation of copper was carried out with different laser powers and the same irradiation time. The UV absorption spectra of the colloidal copper in water were shown in Fig.2

The characteristic absorption peak of copper nanoparticles around 630 nm appeared and shifted a little with the average laser powers of ablation. In our experiments, this plasmon resonance absorption peak position was red-shifted from 629nm to 636nm when average laser power of ablation increased from 200mW to 600mW. According to Mie's theory the resonance peak of nanoparticles is red-shifted when their size increases [4]. The results showed that the laser power density of ablation influences not only the abundance but also the size of nanoparticles. There was no indication of the absorption around 800 nm, which is typical of copper oxide nanoparticles. [5]

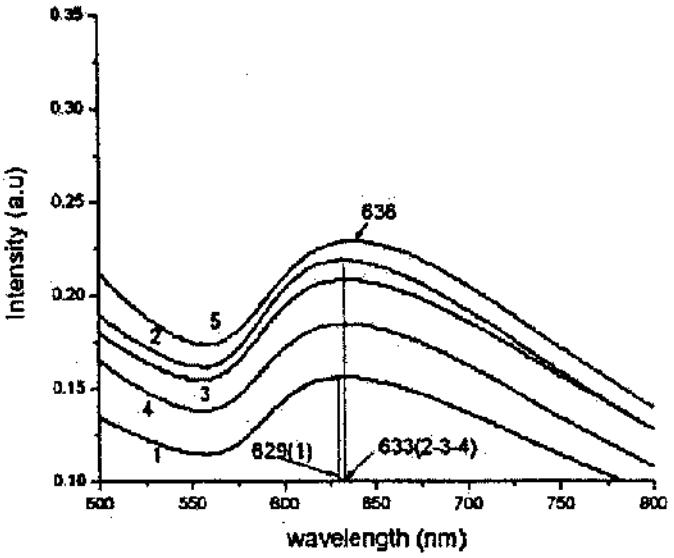

Fig. 2. Absorption spectra of copper nanoparticles in distilled water with the different average laser powers 200 mW (1), 300 mW (2), 400 mW (3), 500 mW (4), 600 mW (5).

The copper nanoparticles produced in water with the average laser power of 200mW was observed by a transmission electron microscope (JEM 1010-JEOL) (Fig.3).

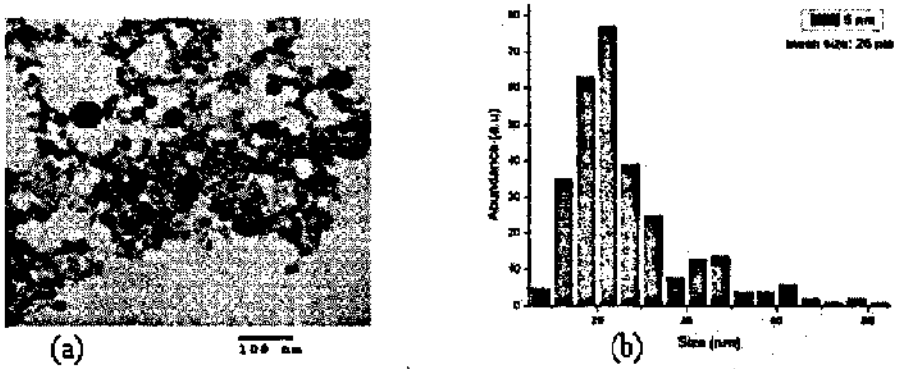

Fig. 3. TEM image (a) and size distribution (b) of copper nanopracticles produced by laser ablation in distilled water.

The TEM image and size distribution exhibit that the size of the particles is around 10-30nm. It was found that the average particle diameter of copper nanoparticles is about 26 nm. The copper nanoparticles colloids prepared in water remained stable for a week.

Then, we carried out ablation of copper in acetone. Figure 4 illustrates absorption spectra of the colloidal copper which were produced in acetone with different laser powers.

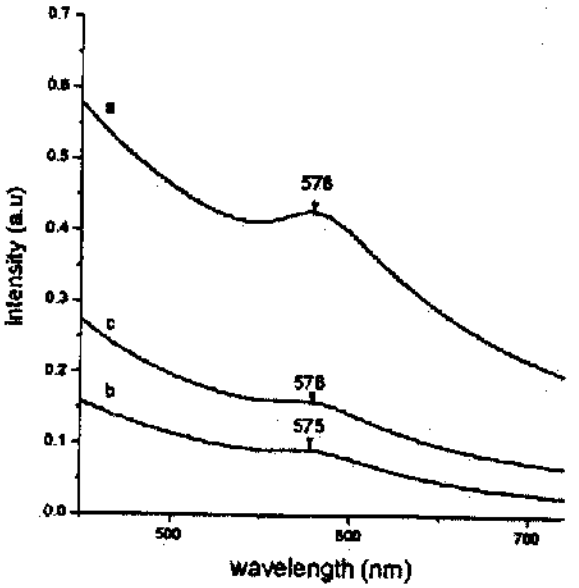

Fig. 4. Absorption spectra of copper nanoparticles in acetone with the different average laser powers 200 mW (a), 300 mW (b), 400 mW (c).

The absorption peak appeared around 580 nm. With laser power of 200 mW, the absorption spectrum has a net shape with peak at 578 nm. The TEM image of copper nanoparticles produced in acetone with laser power of 200 mW was shown in Fig.5a. Copper nanoparticlse are rather spherical in shape.The data of measured size and size distribution of copper nanoparticles were analyzed and given in Fig.5b. It is observed that the diameter of copper nanoparticles concentrate in a range from 2 to 12 nm. The average size of copper nanoparticles is 7 nm. In comparison with the copper nanoparticles prepared in water, the diameter of nanoparticles is smaller and the size distribution is narrower .

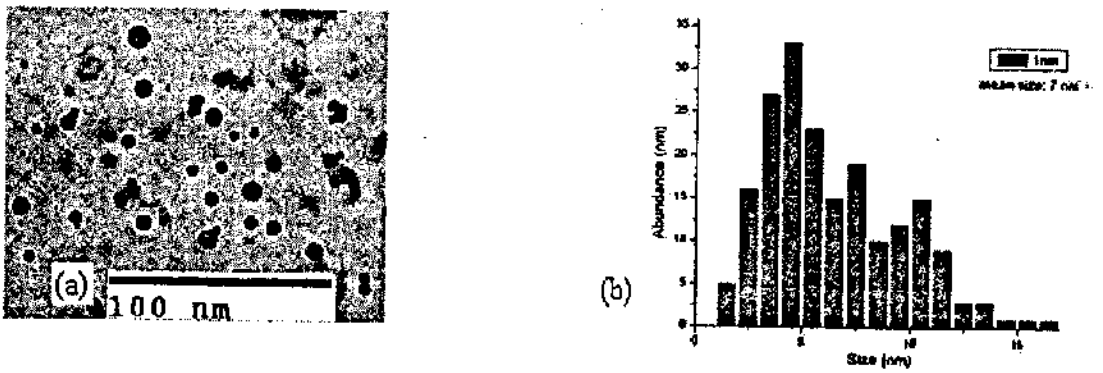

Fig. 5. TEM image (a) and size distribution (b) of copper nanopracticles produced by laser ablation in acetone.

Fig.6 gives a comparison between absorption spectra of Cu nanoparticles prepared in water and acetone by laser ablation using the same laser fluence and irradiation time.

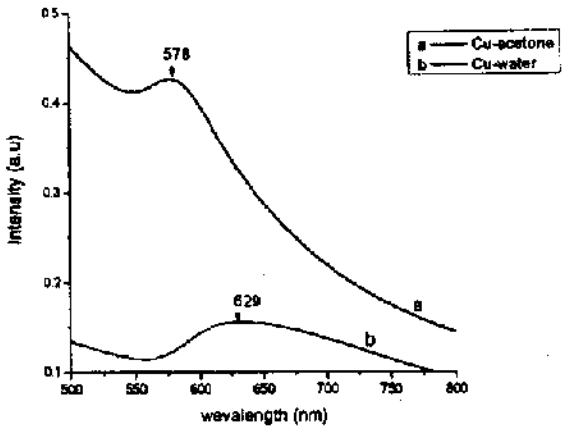

Fig. 6. Absorption spectra of copper nanoparticles in acetone (a) and water (b) with the average laser powers of 200 mW, irradiation time of 15 mins.

The absorption spectra of Cu nanoparticles in water and acetone exhibit a maximum peak at 578nm and 629nm respectively. This result agrees with the average nanoparticle diameter observed from TEM image, 26 nm and 7 nm respectively.

It is known that, in liquids, the nanoparticles are surface-charged. Due to interaction of liquid environment molecules and surface-charged nanoparticles an electrical double layer surrounds the surface of the nanoparticles [6] .Growth rate of nanoparticles depends on the number of particles formed in the first few laser pulses and molecular polarity of liquid environment. Since the molecules of acetone has high dipole moment the electrical double layer surrounding nanoparticles restricted the growth mechanisms during ablation. Hence, in acetone, copper nanoparticle diameter is smaller and size distribution is narrower than those in water. Copper nanoparticles in acetone are stable even after more than two weeks.

4. Conclusion

In the present work colloidal copper nanoparticles were synthesized successfully by pulsed laser ablation of copper targets in water and acetone. Transmission electron microscopy was employed for characterization of the size and shape of the particles. In both media the particles are rather spherical, and it has been found that the average diameters of the copper nanoparticles are 26 and 7 nm in water and acetone respectively. In addition, stability of the colloidal particles were also investigated. The colloidal copper nanoparticles in acetone is stable during 20 days. They were precipitated completely in water after 7 days and colloidal copper nanoparticles change to oxidized particles. Oxidation of copper takes place due to the reaction of dissolved oxygen in water with the colloidal copper nanoparticles. This study also demonstrates a way to control the size of copper nanoparticles by changing the ablation medium.

Acknowledgements. This research was supported by the NAFOSTED Grant N_o 103.02.51.09, Vietnam.

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Studying the role of liquid environments in formation of noble metal nanoparticles by laser ablation

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Abstract. We studied the role of the aqueous solution in formation of noble metal nanoparticles by laser ablation. The gold and silver nanoparticles were produced in different liquids such as water, ethanol, solution of polyvinylpyrrolidone (PVP). Size and optical properties of the nanoparticles were characterized and observed by a transmission electron microscopy (JEM 1010 – JEOL) and UV–visible 2450 spectrometer. In our experiments, we studied the effect of different solution to the average size and stability of the metal nanoparticles against coalescence. Silver nanoparticles prepared in deionized water, ethanol and 0.005 M solution of PVP have average size of 14 nm, 31nm and 12nm respectively. Meanwhile, average size of gold nanoparticles are 21, 24 and 14 nm respectively. The results and discussions will be represented in this report.

Keywords: laser ablation, plasmon resonance, nanoparticles

1. Introduction

Nanoparticles of noble metals have recently become the focus of research because of their unique properties, which are different from those of bulk materials. They have a wide range of optical and electrical properties that originate from quantum confinement effects. These properties depend on the size, shape and material of nanoparticles [1]. Control of size and shape is very important for tuning its properties. The size induced properties of nanoparticles make them suitable for many applications in various areas such as catalysis, optics, and life environments [2]. Numerous physical and chemical methods have been employed to produce metal nanoparticles such as chemical reduction, ultrasonic reduction, radiolytic reduction, etc [3]. Recently, laser ablation method has been developed to prepare nanoparticles with ease and without contamination by a reducing agent. In laser ablation method the nucleation, growth, and aggregation mechanisms depend on several factors including laser wavelength, pulse energy, pulse duration, repetition rate and nature of liquid environments [4]. Liquid environment affect metal nanopaerticle formation mechanism and can be used to adjust the size and shape of nanoparticles. In this work we studied effects of the liquid environment such as water, ethanol and solution of PVP to optical properties, size distribution and aggregation of Au and Ag nanoparticles prepared by laser ablation.

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2. Experimental

We placed a metal plate (99.9 % in purity) in a glass cuvette filled with 10 ml liquid. The fundamental wavelength (1064 nm) of the Quanta Ray Pro 230 Nd:YAG laser in Q-switch mode was focused on the metal plate by a lens having the focal length of 150 mm. The laser was set to give laser pulse with energy of 80 mJ, duration of 8 ns and repetition rate of 10 Hz.

Metal nanoparticles were produced by laser ablation of metal plate immersed in different liquid environments such as water, ethanol, PVP solution. 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 by a Shimadzu UV-2450 spectrometer. The TEM micrograph was taken by 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.

3. Results and discussion

Fig 1 shows absorption spectra of silver nanoparticles produced in deionized water, ethanol and PVP solution.

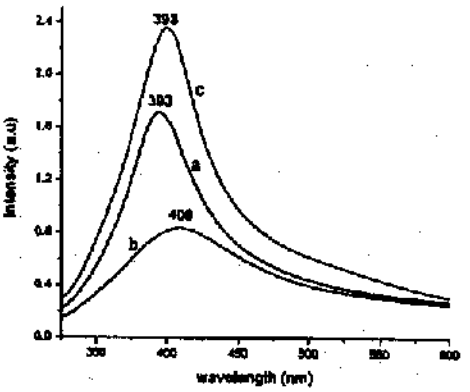

Fig. 1. Absorption spectra of silver nanoparticles
in deionized water (a), ethanol (b) and 0.005 M solution of PVP (b).

The spectra present absorption peaks at visible wavelengths positioned around 400 nm. Optical extinction spectra of samples that were prepared in deionized water, ethanol and 0.005M solution of PVP present extinction peaks at 393, 408 and 398 nm respectively, that can be assigned to the well-known surface plasmon resonance of spherical nanoparticles. The results showed that the optical extinction spectrum of silver nanoparticles in ethanol is broader in comparison with deionised water and 0.005M solution of PVP. The extinction spectra of silver nanoparticles prepared in PVP soltuion is the narrowest. According to the Mie theory of scattering light by small particles, the wavelength of the maximum optical extinction and the shape of the spectra depend on the dielectric function of the medium, size, shape and material type of the nanoparticles [5]. As shown in TEM images, silver nanoparticles are rather spherical in shape. Since the media have similar dielectric functions, the shift

of the maximum of optical extinction is due to a change in the size of the particles. In addition, broadening of the extinction spectra in ethanol is related to the broad size distribution of the particles as confirmed by TEM images.

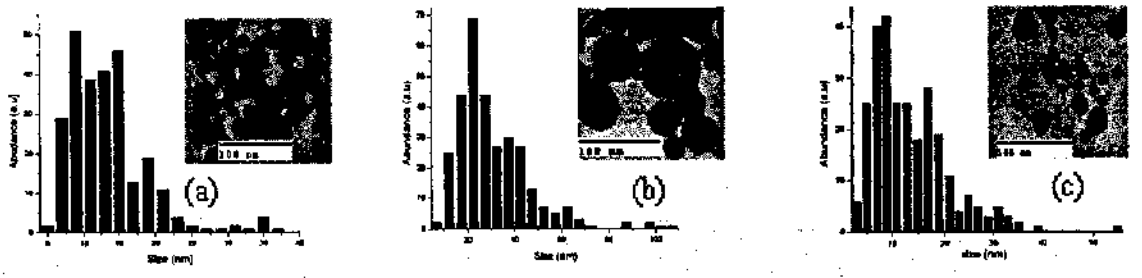

Fig.2. TEM micrograph images and corresponding size distribution of silver nanoparticles prepared in deionized water(a), ethanol (b) and 0.005M solution of PVP(c).

Fig. 2a shows the TEM image and the size distribution of silver nanoparticles prepared in deionized water. Their size distribution is broad with an average size of 14 nm. In ethanol, the size distribution is broadest with a mean diameter of 31 nm (Fig. 2b). Meanwhile, silver nanoparticles produced in the solution of PVP have mean diameters of 12 nm. According to the Mie theory for sphere nanoparticles, the resonance plasmon absorption peak wavelength increasing with particle diameter. The average diameters calculated by TEM images are in good agreement with the absorption spectra (fig.1) where the absorption peaks are red shifted when average size increase .

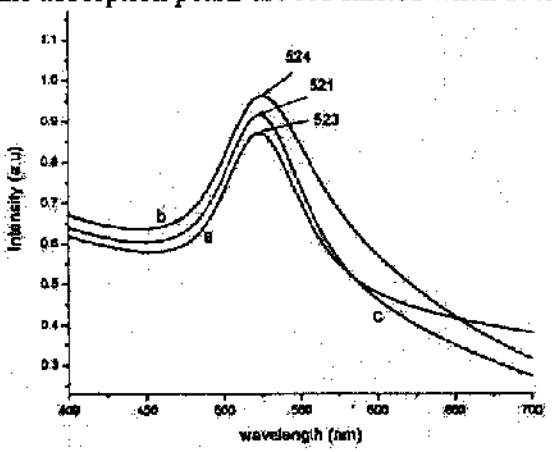

Fig. 3. Absorption spectral of gold nanoparticles
in deionized water (a), ethanol (b) and 0.005 M solution of PVP (c).

We continued to carry out laser ablation of gold in deionized water, ethanol and PVP solution. The absorption spectra, TEM images and size distributions of gold nanoparticles was shown in Fig 3 and Fig 4.

The absorption spectra exhibits the characteristic peak of surface plasmon resonance at around 520 nm. The wavelengths of these absorption peaks are 523, 524 and 521nm in deionized water, ethanol and 0.005M solution of PVP respectively.

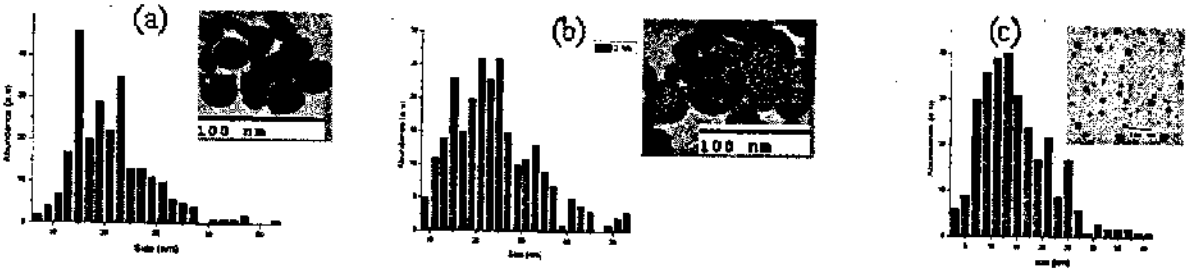

Fig. 4. TEM micrograph and corresponding size distribution of gold nanoparticles prepared in deionized water(a), ethanol (b) and 0.005M solution of PVP (c).

As shown in Fig 4, the prepared gold nanoparticles are rather spherical in shape. Mean size of gold nanoparticles in deionized water, ethanol and 0.005 M solution of PVP are 21, 24 and 14 nm respectively.

The mechanism of pulsed laser ablation of metal in liquids could be explained by a model of Mafune and his coworkers [7]. At first, pulsed laser beam ablates the target during laser irradiation. Ablated materials, which are called plume, expand under liquid environment and disperse many produced species. Dispersed materials include nanopartilces, small clusters, free atoms and ions. For the first few pulses, only liquid medium surrounds the plume and metal species in plume nucleate to produce nanoparticles. The nanoparticles disperse in liquid medium and provide nucleation centers for the next incoming metal species. Plume-nanoparticle interaction takes place. In this stage, two mechanisms contribute to the nucleation process. The first mechanism is direct nucleation of metal in the condense plume similar to the first stage. Another mechanism is addition of the metal species to the nanoparticles that produced before. When both mechanisms occur, broad size distributions will be observed. All attractive and repulsive forces between plume species and nanoparticles such as attractive van der Waals forces and repulsive electrostatic forces due to the overlapping of electrical double layers take a very important role in formation and growth mechanism of nanoparticles.

It is known that, in liquids, the nanoparticles are surface charged. Due to interaction of liquid environment molecules and surface-charged nanoparticles an electrical double layer surrounds the surface of the nanoparticles [7] .Growth rate of nanoparticles depends on the number of particles formed in the first stage and molecular polarity of liquid environment. Molecules with high dipole moment cause more packed and stronger bonds to the surface of the particles. The electrostatic repulsive force due to overlapping of the electrical double layer of the nanoparticles and species in the plume prevents further growth. It was demonstrated that in liquids surface of metal nanoparticles such as Au and Ag is charged negatively because of interaction with medium and different affinity of electron to the surface [6,7]. In water and ethanol the dissociation of OH group on metal nanoparticles results in surface charge and electrical double layer forms. Since the molecule of water has higher dipole moment than pure ethanol, the electrostatic repulsive force restricts more effectively the growth mechanism. As a result smaller Ag and Au nanoparticles and narrower size distribution were observed in water than those in pure ethanol. In order to verify this argument, we carried out laser ablation of Au in solution of ethanol in water with different concentrations.

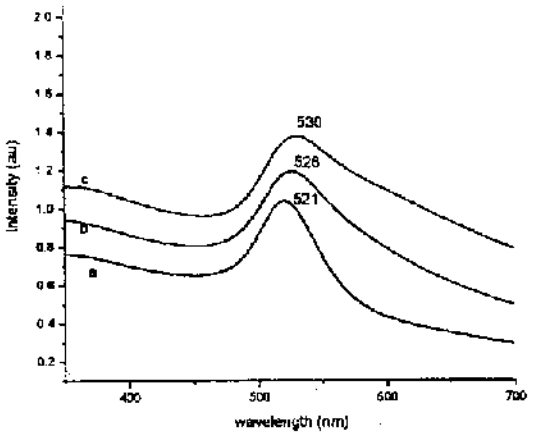

Fig. 5. The absolution spectra of gold nanoparticles colloid prepared in distilled water (a) solution of 30% ethanol (b) and solution of 60% ethanol (c).

Fig. 5 shows the absolution spectra of gold nanoparticles colloid prepared in distilled water, solution of 30% ethanol and solution of 60% ethanol. As obviously seen, when the ethanol concentration increases the absorption spectrum is broaden and absorption peak is shifted to longer wavelengths. The weak electrical double layer due to low polarity of ethanol molecules cause growth and results in the size broadening. We also carried out laser ablation of Ag and Au in distilled water to compare with deionised water. TEM images and size distributions of Ag and Au nanoparticles prepared in distilled water were presented in Fig. 6. The average size of Ag and Au nanoparticles are 9 nm and 13 nm respectively. In comparison with nanoparticles prepared in deionised water, the average diameter of Ag and Au nanoparticles prepared in distilled water is smaller and their size distribution is narrower. These results confirm the role of ions in liquids environment during laser ablation process.

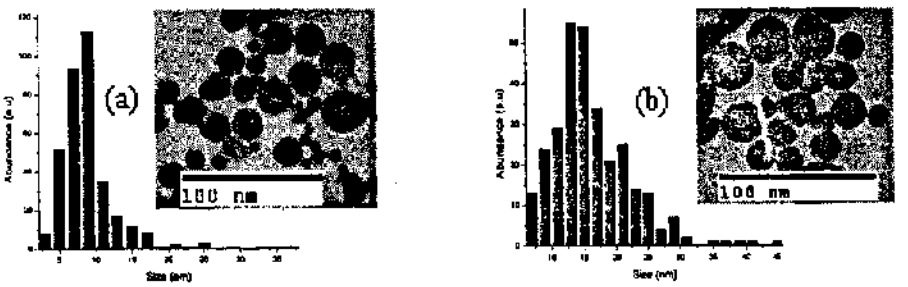

Fig. 6. TEM images and size distributions of Ag (a) and Au (b) nanoparticles prepared in distilled water.

The small size and narrow size distribution of Au and Ag nanoparticles prepared in solution PVP are explained by the role of C=O group of the polymer. In the presence of PVP - $(C_6H_9NO)_n$, the C=O group interact 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. As a result, the metal nanoparticle size is small and dispersion decreases.

4. Conclusion

The role of the liquid environment in preparation of metal nanoparticles by pulsed laser ablation was studied. Silver and gold nanoparticles were prepared in different liquids such as deionized water, distilled water, ethanol and solution of PVP. The TEM and spectral measurements were carried out to determine average size and size distribution of nanoparticles. Our experimental results show that molecular polarity of liquid environment takes a very important role in nanoparticle formation and growth mechanism. High polar molecules provide an electrical double layer, which prevents growth and aggregation. This study support a technique to control average size and size distribution of metal nanoparticles by changing the nature of the liquid environment in pulsed laser ablation.

Acknowledgements. This research was supported by the NAFOSTED Grant N_o 103.02.51.09, Vietnam.

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