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Fabrication and Optical Absorption Properties of Gold - Silver and Gold-Platinum Alloy Nanoparticles Formed by Laser Ablation

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Abstract: Gold, silver and platinum nanoparticles were fabricated by a laser-induced breakdown technique of Au, Ag and Pt metal plates. On the other hand, bimetallic nanoalloys consisting of Au–Ag and Au–Pt have been synthesized by irradiation of the prepared nanoparticles under UV light, which leads to an alloy type of structure. The optical characterization and particle sizes were determined by using absorption spectroscopy and transmission electron microscopy.

Keywords: Nanoparticles, laser-induced breakdown, alloy, bimetal, TEM.

1. INTRODUCTION

Nanoparticles (NPs) of Ag and Au less than 5 nm in diameter are particularly interesting as they may exhibit both classical and quantum size effects in their absorbance spectra [1-3]. Nanoalloys of gold and silver, metals that have essentially identical lattice constants and are completely miscible, present new opportunities to investigate the effect of nanostructure on optical properties [4]. In the case of both gold and silver, with large diameter, D > 5 nm, nanoalloys charge stabilizes in water [5, 6]. Many studies reported the synthesis of various nanoalloys by chemical methods [7-11].

Interest in research on the synthesis of metallic nanoparticles has been evolving due to their amazing properties in catalysis, optics, and electronics [12]. It is known that with the decrease of particle size, particularly to the point where the critical dimensions are in the nanometer regime, many properties can be significantly different from those of their bulk counterparts, especially the catalytic properties [13].

The primary routes to prepare metal nanoparticles include reduction, which is carried out by employing a powerful reducing agent, such as sodium borohydride (NaBH4), in the presence of a stabilizer [14]. The excess use of NaBH4 may result in the adsorption of unused BH3 ions onto the nanoparticle surface resulting in the contamination of borides on the nanoparticle surface. Furthermore, as the phase transfer agent and the stabilizer are sometimes chemically different, a long postsynthesis purification procedure is still an issue in this technique. At this point, irradiation-based synthesis becomes a good choice due to the advantage of being free from preadded reducing agents.

Reduction of metal ions is facilitated by an abundance of high-energy electrons and radicals created in situ through the ionization and excitation of solvent molecules by radiation. Nanoparticle synthesis using an intense γ ray [15] has been explored as a key method in irradiation-based techniques for the past two decades, while synchrotron X-ray [16, 17] and femtosecond laser [18-26] techniques have recently attracted much attention due to the identical process underlying the reduction process of metal precursors to zero valence nanoparticles. In particular, water molecules have been reported to be decayed by femtosecond laser techniques via two-photon absorption, generating solvated electrons and hydrogen and hydroxyl radicals along with dissociation products such as hydronium ions and H2O+. at decimolar concentrations [27]. Furthermore, exposing the system to different additives such as dispersants and ion scavengers will generate a series of reducing radicals with different reduction potentials, which can reduce metal precursors selectively. Even though γ-ray and synchrotron X-ray irradiation sources are very efficient, these methods have some drawbacks, such as radioactivity and poor accessibility. From this viewpoint, a laser-induced breakdown irradiation method seems to be more promising due to its simple, safe and “green” properties. Using a 100 mJ/pulse, we report the formation of Au, Ag and Pt nanoparticles in distilled water. Gold is very useful as an alloying metal in conjunction with other metals, and the structure of bimetallic combinations depends mainly on the preparation conditions and the miscibility of the two components [28]. Combinations such as Au–Pd and Au–Pt have been reported to exhibit a core-shell structure while Au–Ag forms either a core shell or an alloy [29]. Cheng et al. (2011) have also investigated an Au–Pt system in which they found that the fabricated particles were alloys but possessed a broad size distribution with an average of about 15 nm. They suggested that this might be because of the midlevel laser pulse energy used in this work or because of the miscibility gap of Au and Pt systems for making a solid solution [30].

In the present study, we fabricated gold nanoalloys with silver or platinum in an effort to combine the optical properties of the noble metal alloys. These nanoalloys can be conjugated with functional groups and applied in biosensing as extremely pure and efficient sensors. We report the fabrication of gold nanoparticles by laser ablation of a gold metal plate in different solvents of different physical properties. In addition, we have investigated the formation of Au–Ag, Au–Pt and Ag–Pt alloy nanoparticles.

2. EXPERIMENTAL SECTION

2.1. Materials and Methods

Gold, silver and platinum (>99.9%, Fluka) nanoparticles were prepared by laser ablation of the corresponding metal plates. The ablation in the case of gold was carried out in different solvents (purse, Fluka). Double distilled water was used. As shown in Fig. (1), the metal plate was placed on the wall of a quartz cuvette filled with 3 mL of solvent. Laser pulses (τ = 8 ns at 10 Hz) from a Nd:YAG laser (continuum SLI-10) at λ = 1064 nm were focused onto the surface of the metal plate using a fused silica cylindrical lens (p = 100 nm).
The spectra illustrated a plasmon absorption band at $\lambda_{\text{max}} = 522$ nm. Fig. (3) shows the absorption spectra of gold nanoparticles prepared by laser ablation in different solvents.

3. RESULTS AND DISCUSSION

3.1. Fabrication of Au Nanoparticles in Different Solvents

Fig. (2) shows the absorption spectra of the spherical gold nanoparticles prepared by the chemical method in distilled water [19].

The spectra illustrated a plasmon absorption band at $\lambda_{\text{max}} = 522$ nm. Fig. (3) shows the absorption spectra of gold nanoparticles prepared by laser ablation in different solvents.

Additionally, the photographs of the irradiated solutions are presented in the inset of Fig. (3), where the colors clearly indicate a gradual variation in the gold SPR peak. The spectra are characterized by different positions of the maximum absorption bands depending on the solvent polarity as shown in the figure. Fig. (3) also shows that the absorption band for Au NPs in water is similar to that shown by Turkevich [31] (Fig. (2)). It is well known that the plasmon absorption position of the gold nanoparticles is dependent on the polarity of the surrounding solvents [32]. The greater the value of the solvent polarity, the greater the interaction between the nanoparticles and the solvents, which results in high dispersion of the particles. This might be due to the fact that the interaction between the nanoparticles and the polar solvent is more favorable than particle-particle interactions. The results showed red shifts by ~69 nm after decreasing the solvent polarity from water ($\lambda_{\text{max}} = 522$ nm, polarity=9) to THF ($\lambda_{\text{max}} = 591$ nm, polarity=4) (polarity order H$_2$O > CTAB > EtOH > THF [33]). In other words, the higher the dipole moment (H$_2$O=1.85 Debye), the higher the particles dispersion and the lower the dipole moment (THF=1.65 Debye) [34] the lower the particle dispersion. As shown in Fig. (3), the absorption spectra of nanoparticles in THF were broad and extended. The broadening of the spectra may be due to the particle-particle interaction since in less polar (small dipole moment) solvents the ability of nanoparticles to aggregate is higher than the interaction between the solvent molecules and the nanoparticles [22]. In the case of the chemical method, the capping materials might be preventing the nanoparticles from aggregating, unlike those prepared by laser ablation.

3.2. Fabrication of Au–Ag Nanoalloys

Fig. (4) shows the absorption spectra of gold and silver nanoparticle mixtures (Fig. (4a)) and nanoalloys (Fig. (4b)). The spectra in Fig. (4a) represent a physical mixture of the individual Ag and Au particles. It shows two plasmon peaks corresponding to the monometallic counterparts, the first one at $\lambda_{\text{max}} = 403$ nm for silver and the second at $\lambda_{\text{max}} = 522$ nm for gold. After irradiation of the bimetals mixture for 1 hour, the UV-visible spectroscopy study was carried out (Fig. (4b)), and the optical absorption spectra show only one plasmon peak for the bimetals located at $\lambda_{\text{max}} = 508$ nm, confirming the formation of bimetallic Au–Ag alloy nanoparticles.

It is known from the literature that alloy NPs of two metals show an absorbance peak between those of the two individual nanoparticles [24]. Thus, the obvious red shift of the silver nanoparticle peak provides strong evidence of the formation of a Au–Ag nanoalloy. The shape and size of the resultant nanoparticles are elaborated with TEM. The TEM images and the particle size distribution of Au–Ag alloy nanoparticles are presented in Fig. (5a and 5b). The particles are nearly spherical with high uniformity in size.
and are well separated. The mean diameter of Au–Ag alloy nanoparticles was about 10 nm.

These results are in strong agreement with the UV–vis spectroscopic data discussed previously and the reported data [35].

The Laser radiation has identical process underlying the reduction process of metal precursors to zero valence nanoparticles. Particularly, water molecules have been reported to be decomposed using lasers, generating solvated electrons, hydrogen and hydroxyl radicals, along with dissociation products such as hydronium ions and $\text{H}_2\text{O}^+$ that can reduce metal precursors selectively [16].

3.3. Fabrication of Au–Pt Nanoalloys

In the case of Au–Pt nanoalloys, the optical spectra of the gold nanoparticles along with the spectrum of Pt nanoparticles alone produced under similar conditions to those of the Au–Ag NPs are shown in Fig. (6).
The Au nanoparticles alone display a peak at $\lambda_{\text{max}} = 522$ nm while platinum particles show only a monotonous increase in absorbance as the wavelength decreases [36]. For Au–Pt alloy NPs, a peak at 518 nm is observed with small blue shift, and the decrease in the optical density peak compared to the gold NPs suggests the formation of alloy NPs by the optical characterization. For further confirmation of alloy formation, the alloy NPs were subjected to TEM characterization. Fig. (7) indicates that the NPs are mostly polydisperse in nature with an average size of $\sim 5-10$ nm $\pm 0.5$, and some alloy particles tend to form aggregates due to the absence of a capping material [37].

When the particles become several nanometers in size, most of the atoms generated by the laser irradiation are expended so that particle growth may be terminated [18].

4. CONCLUSIONS

We prepared Au, Ag, and their bimetallic nanoparticles using Nd-YAG laser irradiation of metal plates in distilled water. Metal nanoparticle formation by femtosecond laser irradiation and the nonlinear optical properties of Au–Pt alloy NPs by the optical characterization. For further confirmation of alloy formation, the alloy NPs were subjected to TEM characterization. Fig. (7) indicates that the NPs are mostly polydisperse in nature with an average size of $\sim 5-10$ nm $\pm 0.5$, and some alloy particles tend to form aggregates due to the absence of a capping material [37].

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CONFLICT OF INTEREST

The authors confirm that this article content has no conflicts of interest.

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Declared none.

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