Fabrication and Optical Properties of Ag-Au Alloy Nanoparticles

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Abstract

Background/Objectives: Methods for the synthesis of Ag-Au alloy nanoparticles have received considerable attention due to their special characteristics and applications. Among different synthesis methods for alloy nanoparticles, high-voltage wire explosion of twisted wires has significant advantages for manufacturing production. Method/Statistical Analysis: In this work, Ag-Au alloy nanoparticles were synthesized by a high-voltage electrical explosion of twisted wires (of Ag and Au) in deionized water for the first time. The compositions of obtained nanoparticles were changed by adjusting the cross-section ratio of Ag and Au twisted wires. Finding: The obtained nanoparticles were characterized by applying X-ray diffraction (XRD), transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS) techniques. Localized surface plasmons resonance (LSPR) of Ag-Au alloy nanoparticles were studied by UV-vis spectroscopy and it was found that the position of the LSPR band of the nanoparticles could be tuned by the variation of their composition linearly. Conclusion/Application: Among different synthesis methods, high-voltage EEW has higher efficiency in industrial production of metallic nanoparticles, and using twisted wires in this method is a good substitution of pre-Alloyed and electrodeposited wires for fabrication of alloy nanoparticles.

Keywords: Ag-Au Alloy Nanoparticles, High Voltage, LSPR, Twisted Wires, Wire Explosion

1. Introduction

Numerous studies have focused on different methods for producing alloy nanoparticles, including arc discharge¹, laser irradiation²-⁵, chemical process⁶-⁸, green methods⁹, etc. Among various alloy nanoparticles, Ag-Au alloy nanoparticles have received more attention due to their special characteristics and applications such as catalysis¹⁰,¹¹, electronics¹², plasmonic devices¹³,¹⁴, electrochemical sensing¹⁵, and surface enhanced Raman scattering¹⁶ (SERS). Considering the fact that Ag-Au alloy nanoparticles’ properties depend on their composition, tuning the composition is an outstanding facility for synthesis methods and there are many reports explaining this facility. Laser irradiation has been used to produce Ag-Au alloy nanoparticles during the past years. Have synthesized homogenous Ag-Au alloy nanoparticles using bulk alloy metals, so that the composition of their nanoparticles showed very good agreement with the primary bulk alloy metals². Have produced Ag-Au alloy nanoparticles using laser irradiation of a mixture of individual monometallic Ag and Au colloids and studied exposure time of irradiation (0-4h)⁷. Have also mixed pure Ag and Au colloids at different volume ratios, and then used laser irradiation of the mixture colloids to produce alloy nanoparticles in varied compositions. In order to control the composition of obtained alloy Ag-Au nanoparticles, the volume ratio of initial Ag and Au colloids were adjusted⁴. However, the major restrictions of this method are expensive laser equipment required and time-dependency of the synthesis performance. Co-reduction of HAuCl₄ and AgNO₃ is the other common method to prepare Ag-Au alloy nanoparticles have used this chemical method with different reducing and capping agents⁶-⁸. This method provides

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a good opportunity for tuning the alloy nanoparticles composition, but due to the expensive initial chemical materials, these methods are not good for industrial production. Furthermore, owing to the application of nanoparticles, they are highly regarded for mass production. Recently, electro-exploding wire (EEW) technique has been used for fabrication of the metallic nanoparticles. Using the EEW technique, a high magnitude of current passes through a metal wire in a short time and converts the wire to a vapor state. The vaporized metal is then cooled down instantaneously to form nanoparticles. High rate of production, short reaction time, no need for expensive chemical materials and high-priced equipment such as vacuum pump, laser, etc could be mentioned as the advantages of EEW technique. Because of these advantages, nanoparticles produced by an EEW method are most broadcasted in the world market. This technique is widely applied to the synthesis of alloy nanoparticles using two kinds of wires: pre-alloyed wires and electrodeposited ones. Used FeNi3 pre-alloyed wires to synthesis FeNi3 permalloy nanoparticles and composition of obtained nanoparticles are reported as agreed with pre-alloyed wire. Used the explosion of Cu-plated Ni wire to produce single phase CuNi alloy nanoparticles. A motor-driven pulling system was applied to ensure uniform thickness of the Cu layer deposited on Ni wire, and Ni wire was pulled at a controlled speed through the Cu plating bath. The compositions of obtained nanoparticles were controlled by altered pulling speed and applied voltage during electrode position process.

Using pre-alloyed wires is limited to the wires commercially available in the market and electrodeposited wires are difficult to be prepared. However, using the twisted wires is very simple solution for alloying nanoparticles in EEW, synthesized Ni-Cu alloy nanopowder in nitrogen and argon ambient while controlling the composition of the nanopowders by changing the ratio of Ni to Cu wire diameter. Prepared Ti-Fe nanoparticles by wire explosion of twisted wire (including ten wires) and controlled nanoparticles’ composition by adjusting the number of Ti and Fe wires in the twisted wire.

Applying high-voltage explosion of twisted wire method in liquid media such as distilled water can cost less than gas ambient.

There isn’t any report for the synthesis of Ag-Au alloy nanoparticles using high-voltage EEW, hence the synthesis of Ag-Au alloy nanoparticles by high-voltage EEW is reported herein for the first time. However, fabricated Ag-Au alloy nanoparticles by a kind of EEW that is referred herein as low-voltage EEW to distinguish it from the usual type (high-voltage EEW). In their work, Au and Ag wires with the same diameters were jointed, and a low voltage of 12 V was applied between the jointed wires (as anode) and a silver plate (as cathode), a spark is taken place, and Ag–Au alloy nanoparticles synthesized. High ratio of silver to gold composition of the obtained alloy nanoparticles was observed, despite of being jointed wires in the same diameters. It may be considered as the effect of silver plate. In turn, in the present study, the high-voltage method was used and the percentage of Ag to Au synthesized alloy nanoparticles in composition was agreed with the cross-section ratio of the Ag and Au twisted wires.

In this paper at first, the Ag-Au alloy nanoparticles were synthesized by applying 400V on the twisted Ag and Au wires in deionized water (high-voltage wire explosion). The synthesis process was performed using plasma nano colloid (PNC1k, Nano Engineering and Manufacturing Co. (PNF Co.), Iran). After that, the obtained nanoparticles were characterized by XRD, TEM and EDS. Considering the applications of the noble metallic nanoparticles in plasmonics, the importance of studying the effect of alloying on localized surface plasmon resonance (LSPR) of the nanoparticles will be vivid. LSPR of the obtained nanoparticles were investigated by UV-vis spectroscopy, and then compared with each other.

2. Material and Methods

Ag and Au wires were made from the irbullion (99.99%) and were thinned using durston-rolling-mill and draw-plates (diameter: 0.24mm, 0.21mm, 0.17mm and 0.12 mm). Five kinds of wires were prepared that summarized in table 1 as samples 1-5. Ag and Au wires with diameters 0.24mm were used for synthesis of the pure Ag and Au nanoparticles (1 and 5 samples). To synthesis the alloy nanoparticles, the Ag and Au wires of different diameters were hand-twisted tightly (samples 2-4).

Then, the twisted wires were guided by a nozzle into the vessel and were installed between the high-voltage electrodes (Figure1). The stainless steel disc, 10cm in diameter and 3mm in thickness, was used as anode and a stainless steel cube (25*10*3mm³) with a circular hole (5mm diameter) inside it was used as a cathode and the distance between the electrodes was adjusted to 5mm. The length of the loaded wire between the electrodes for
Table 1. The summary of the characteristics of twisted wires.

| Ratio cross-section of Au to total wires | Total cross-section of the Au wires | Material and diameters of wires | Sample No |
|----------------------------------------|------------------------------------|--------------------------------|-----------|
| 1                                      | 0.045 mm²                          | Au wire with diameter 0.24 mm  | 1         |
| 0.75                                   | 0.034 mm²                          | Au wire with diameter 0.21 mm, Ag wire with diameter 0.12 mm | 2         |
| 0.50                                   | 0.022 mm²                          | Au wire with diameter 0.17 mm, Ag wire with diameter 0.17 mm | 3         |
| 0.25                                   | 0.011 mm²                          | Au wire with diameter 0.12 mm, Ag wire with diameter 0.21 mm | 4         |
| 0                                      | 0                                  | Ag wire with diameter 0.24 mm  | 5         |

each explosion was 1 cm, so wire was connected to two electrodes before the explosion.

The electrodes were connected to a capacitor bank of 500 μF through a plasma switch and the pet was filled with ~1 lit of deionized water. A 400 V voltage was applied to the twisted wires. Then, very strong pulse current passed through the wire, resulting in an explosion and production of colloidal nanoparticles in water. Finally, the colloid of alloy nanoparticles was characterized by TEM, XRD and EDS. Optical absorption of obtained nanoparticles were investigated by UV-vis spectroscopy, and then compared with each other.

3. Results and Discussions

3.1 XRD Patterns

The dried powder of the nanoparticles was obtained by freeze-drying after centrifugation at 3600 rpm. The structural investigation of the powder was performed by an X’Pert Pro MPD X-ray diffractometer using CuKα1 radiation (λ = 1.54060 Å).

The obtained XRD patterns are shown in Figure 2 the observed peaks indicated that all products were formed as a face-centered cubic (fcc) structure. For example, the observed peaks in Au pattern were at two theta degrees of 38.42, 44.60, 64.83, 77.85, and 82.01 corresponding to the {111}, {200}, {220}, {311}, and {222} planes of the fcc structure.

XRD analysis is a precise tool to confirm alloy formation. The amount of lattice parameters of the Ag and Au are almost the same (aAg = 4.09 Å, aAu = 4.08 Å for bulk[25]) and the positions of their XRD peaks are so close. In such cases, the researchers use accurate scanning of the peaks in order to look for a probable doublet[24]. No splitting was observed in scanning of the all peaks. One of these peaks (111) in the range of 37 to 40 degrees is shown in the inset of Figure 2. It is confirmed that this method (in the case of the Ag and Au twisted wires) leads to forming the Ag-Au alloy nanoparticles and does not make the Au and Ag nanoparticles separately. The lattice parameters of products were calculated as being 4.054, 4.060, 4.066, 4.071, 4.074 Å for samples 1 to 5, respectively. Increasing of lattice parameters (from 4.054 Å for Auto 4.074 Å for Ag) is related to a reduction in Au contents (increasing of Ag contents) in products. It should be mentioned that the lattice parameters of obtained Ag and Au nanoparticles (samples
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Figure 2. XRD patterns of the obtained nanoparticles (samples 1-5) and the inset image shows a zoom of the (111) peaks.

1 and 5) are smaller than their lattice parameter reported for their bulk. Some researchers conducted comparative studies to see the differences in the lattice parameters between the bulk and nanostructure forms of materials. Their results show that the lattice parameters of the nanoparticles are smaller than the bulk of the same materials. Our results are in agreement with their reports.

3.2 TEM Images

Morphology of the alloy nanoparticles (sample 3), for example, was studied using TEM (Phillips CM-30, running at 150 kV). Sample preparations were performed by placing drops of sonicated colloidal solution on a copper grid. Then, by using a blotting paper, the excess solvent was removed and after that, letting the remaining solvent evaporates at room temperature.

Figure 3 shows the TEM image of the Ag-Au alloy nanoparticles (sample 3). The nanoparticles are nearly spherical and the particles' size distribution is broadened from 2 to 25 nm with the average size (D) of 12.5 nm.

3.3 EDS Analysis

The compositions of the products were investigated using energy dispersive spectroscopy (EDS: VEGA\TESCAN-LMU). The EDS spectra for sample 3 is shown as an example in Figure 4. The dried powders used for XRD analysis were prepared for this analysis too. The EDS results indicated that the Au, Ag\textsubscript{0.27}Au\textsubscript{0.73}, Ag\textsubscript{0.54}Au\textsubscript{0.46}, Ag\textsubscript{0.79}Au\textsubscript{0.21} and Ag present in the samples 1-5, respectively. One can easily estimate the alloy composition of the nanoparticles according to the closed lattice parameters of Ag and Au, and also the cross-section ratio of their twisted wires.

Although the Ag concentrations of the obtained samples were a little higher than the estimated values, the composition of the nanoparticles evaluated from the EDS analysis was nearly in agreement with the estimated value (8, 8 and 5.33 percentage difference for samples 2-4, respectively). Furthermore, from Figure 4 one can see that there aren’t any considerable impurities from the electrodes, and also the existence of oxygen peak is likely due to the oxidation of atoms on the surface. Prepared
jointed wires with similar cross-section too, but their XPS analysis revealed the Ag$_{80}$Au$_{20}$ composition for obtained alloy nanoparticles$^{24}$. This shows that in their work, the silver plate (as cathode) has a strong effect on the composition of the nanoparticles.

It should be noted that the facility of tuning the composition of products in high-voltage EEW twisted wires method were indicated very well before. For example, synthesized Ni-Cu alloy nanopowder in nitrogen and argon ambient using high-voltage EEW twisted wires. They used Ni (with purity 99%) and Cu (with purity 99.9%) single wires that were twisted together to form a stranded wire. The ratio of the Ni to Cu wire diameter was varied to adjust the Cu content in the standard wire to be 0, 19, 48, 68, and 100 mol% Cu. EDS analysis exhibited good agreement between the Cu content of nanoparticles and standard wires$^{21}$.

### 3.4 UV-Visible Spectroscopy

Noble metal nanoparticles received great interest because of their strong localized surface plasmon resonances (LSPRs). The LSPR peak of the metal nanoparticles is sensitive to the nanoparticles’ size, shape, and composition. Here, the effect of alloying on LSPR of nanoparticles was examined. UV-visible spectroscopy is a convenient technique for evaluating LSPR wavelength of the nanoparticles in aqueous phase. Figure 5 showed absorption spectra of the obtained colloidal nanoparticles yield by Shimadzu UV-1800 spectrometer.

A significant issue in the absorption spectra of the Ag-Au alloy nanoparticles is that only one peak is observed. In some literatures from the comparison between the alloy nanoparticles and mixed of the pure nanoparticle one can confirms the alloy phase formation$^{3,4,24}$. For example, investigation LSPR of the mixed colloid of the pure Ag and Au nanoparticles, observed two distinct peaks in 400 and 550 nm corresponding to the pure Ag and Au nanoparticles, respectively. Then, they exposed the mixed colloids under laser irradiation and studied the effect of irradiation time on absorption spectra of the colloid. By increasing the exposure time up to 4 h, the results showed that the two distinguished peaks have been converted into a unique peak around 490-495 nm which is related to the formation of the Ag-Au alloy nanoparticles$^{3}$.

In our work, the absorption spectra of the nanoparticles exhibited a single peak for each sample as shown in Figure 5. In this figure, the single peak for the samples can be seen around 395, 424, 451, 489 and 522nm corresponding to Ag, Ag$_{0.79}$Au$_{0.21}$, Ag$_{0.54}$Au$_{0.46}$, Ag$_{0.32}$Au$_{0.68}$ and Au nanoparticles, respectively. The LSPRs of Ag$_{1-x}$Au$_{x}$ nanoparticles (x is Au mole fraction of nanoparticles) exhibited red shift from 395 to 522 nm with the increase of x in linear behavior (inset of Figure 5).

In general, being LSPR peaks as single and a linear relationship between the wavelength of the maximum absorption spectra ($\lambda_{\text{max}}$) plotted vs. the Au mole fraction of samples.

5. Conclusions

Among different synthesis methods, high-voltage EEW has higher efficiency in industrial production of metallic nanoparticles, and using twisted wires in this method is a good substitution of pre-Alloyed and electrodeposited wires for fabrication of alloy nanoparticles. In present work, Ag-Au alloy nanoparticles were synthesized by the high-voltage wire explosion of twisted silver and gold wires in deionized water, for the first time. The obtained alloy nanoparticles were characterized by XRD, TEM, EDX and UV-visible spectroscopy. XRD analysis confirmed the formation of nanoparticles in the alloy phase in the
products related to Ag and Au twisted wires. Increasing of the lattice parameters from 4.054 Å for Au to 4.074 Å for Ag was observed, which is corresponding to the increasing of Ag contents in samples. TEM images showed the spherical morphology of the nanoparticles with the average size of 12.5nm. The composition of the nanoparticles evaluated from the EDS analysis nearly agreed with estimated value according to the cross-section ratio of the twisted wires (Ag and Au wires). UV-visible spectroscopies were used to examine the effect of alloying on LSPR of nanoparticles. The LSPRs of the Ag$_{1-x}$Au$_x$ nanoparticles exhibited a red shift from 395 to 525 nm with the increase of x in linear behavior. The existence of a single LSPR peak and a linear relationship between the wavelengths of LSPR of the Ag$_{1-x}$Au$_x$ (Lmax) with x were good evidence for the formation of the Au-Ag alloy nanoparticles.

6. Acknowledgements

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7. References

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