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Preparation of gold nanoparticles by arc discharge in water

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Abstract

Gold nanoparticles have been attracting attention due to their extensive application in chemistry, physics, material science, electronics, catalysis and bionanotechnology. Synthesis of gold nanoparticles often involves toxic and expensive physical-chemistry methods. Preparation of gold nanoparticles by arc discharge in water is proposed for the first time. Fabrication of gold nanostructures in deionized water has been successfully established. The evidence of gold particles' light absorbance reveals a unique surface plasmon resonance for Au nanoparticles suspended in deionized water. Gold nanostructures uniformly dispersed in water, their UV–Vis absorption and crystalline size are shown. Our experimental results demonstrate that fabrication of gold nanoparticles by arc discharge in water is an alternative, cheap, effective and environmentally friendly method.

Keywords: Gold; Nanostructured materials; Nanofabrications; SEM; XRD

1. Introduction

Metal nanoparticles have often been studied and used in nanotechnology. In particular, gold nanoparticles have been widely studied aiming at a variety of applications, such as catalysis, biolabeling, nonlinear optical devices, and optical recording media.

Current techniques used to produce gold nanoparticles are usually divided into chemical and physical methods. Chemical methods usually involve toxic chemicals which can be dangerous for our environment. Physical methods include UV and IR radiation, aerosol technology and lithography [1–3]. Although these methods may successfully produce pure gold nanoparticles, they require the use of some stabilizers protecting Au nanoparticles against agglomeration. These methods may remain quite expensive and potentially dangerous for our environment.

Our studies have shown that DC arc discharge in water is a good alternative to the other methods and is relatively cheap and environmentally friendly. As far as we know, there is no scientific literature describing Au nanoparticles being produced by arc discharge in pure water. During arc discharge, where the temperature between electrodes can reach several thousands of degree Celsius [4], the Au wires are etched in the water medium. The vaporized metal can be condensed more efficiently in the dielectric liquid than in a gas phase. Gold vapor condensed in water creates a stable Au aqueous suspension. Well-separated nano-size Au clusters in pure water seem to be thermodynamically stable for a long time.

2. Experimental

2.1. Materials

Gold wires (Gredmann, 99.99%) 1 mm in diameter were used as electrodes submerged in deionized water (pH = 6.5, conductivity = 0.8–0.9 μS).

2.2. Experimental system

The DC arc discharge system (Fig. 1) consists of four main parts: (i) two gold electrodes, (ii) a servo control system which can maintain a constant distance

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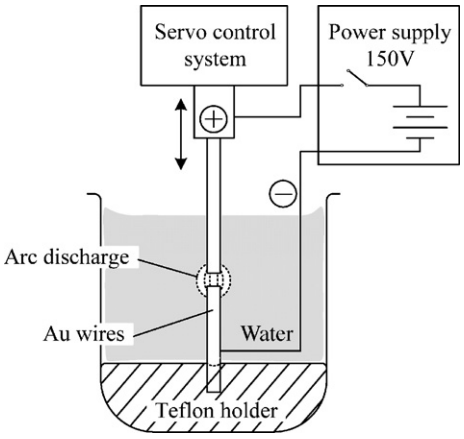

Fig. 1. DC arc discharge system.

between electrodes, (iii) a power supply system which can control the DC arc discharge parameters and (iv) a glass container with Teflon electrode holder and deionized water to collect the gold colloid.

2.3. Preparation of the water suspension with gold nanoparticles

The power supply system provides a stable pulse voltage to etch the Au electrodes in water. To ionize the aqua medium between the electrodes the DC arc discharge system provides pulse voltage of around 70–100 V for 2–3 μs and then a pulse of 20–40 V is maintained for around 10 μs. In this time the etching current can reach 4 A. Well-controlled time on and off is shown in Fig. 2. The servo control system based on a feedback loop controls the gap between electrodes which is equal to a few microns. The upper Au electrode is held by the servo control system and the bottom one is fixed by the Teflon ring. The container with deionized water was maintained at room temperature.

Gold wires were used as both the positive and negative electrodes. The pure gold wires were etched by the DC pulse arc discharge in water. The parameters of the control system were chosen to obtain the optimal conditions to produce Au nanoparticles.

The governing parameters of this system, such as the applied working voltage, selected electric current, pulse duration (on/off-time), electrode gap, temperature of the deionized water, are crucial factors for nanoparticles production. During the arc discharge the surface layer of the Au wires was evaporated and condensed in the water, creating a gold suspension. Then colloidal gold was collected for inspection and analysis to determine the Au particle size distribution, the particles' zeta potential and optical properties.

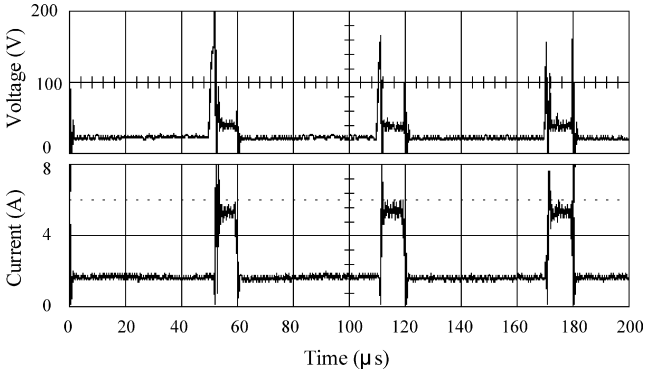

Fig. 2. Current and voltage pulses created by the DC arc discharge system during etching of the gold electrodes.

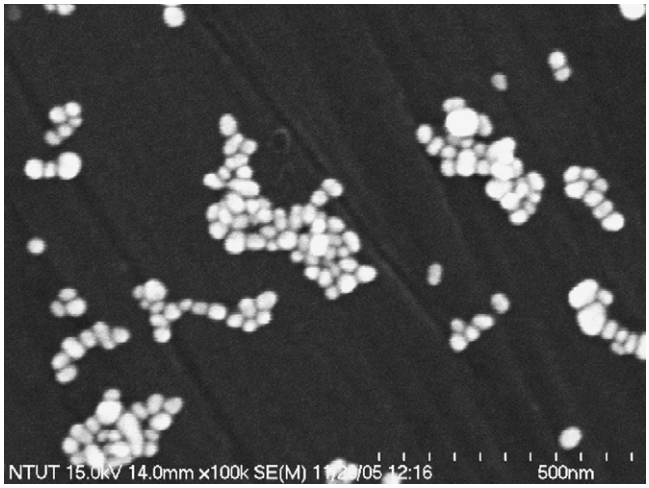

Fig. 3. SEM image of the gold nanoparticles.

2.4. Au nanoparticles characterization

The field emission scanning electron microscope (FE-SEM, HITACHI S4700) was used to determine the gold nanoparticles size distribution. The EDX spectrum was taken to demonstrate the chemical composition of the Au particles. The Zeta potential of the aqueous suspension of charged Au particles was measured by the NanoZS90 system (Malvern) and was determined based on the velocity of a particle in a unit electric field. A double-beam UV–Vis spectrophotometer (9423UVA1002E Helios Alpha) was used to analyze the optical properties of the Au nanoparticles.

3. Results and discussion

Fig. 3 depicts the SEM image of the gold nanoparticles. Several drops of gold colloid were deposited on a conductive silicon wafer and then the sample was gently heated on a heating plate. The secondary electrons SEM image was taken. Fig. 4 shows the size distribution of the gold nanoparticles calculated from the SEM image. As one can notice, Au particles with size included in the range of 15–30 nm dominate.

The EDX spectrum (see Fig. 5) was obtained from the same gold colloid sample as that for SEM. It demonstrates the distinct

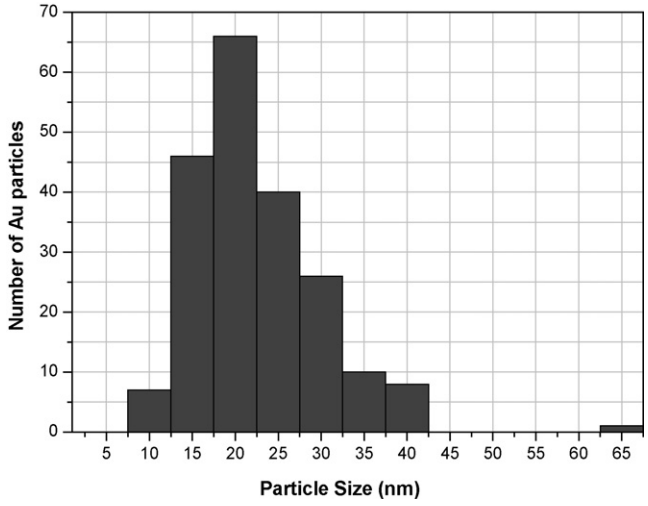

Fig. 4. Size distribution of the Au nanoparticles calculated from the SEM image.

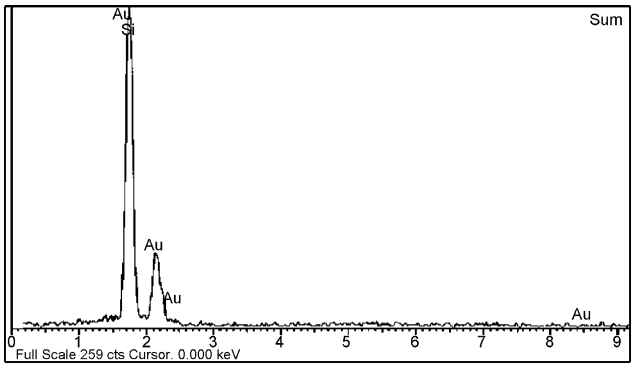

Fig. 5. EDX spectrum of the Au nanoparticles deposited on the silicon wafer.

presence of gold peaks at 1.87, 2.1213 keV (Au Mα), 2.149 keV (Au $K\beta_1$) and 2.205 keV (Au Mβ). Also we can find the Si peak at 1.7398 keV (Si Kα) due to the presence of the silicon wafer used as a support for Au nanoparticles.

Zeta potential for gold colloid with maximum at around −35 mV (Fig. 6) shows negatively charged Au nanoparticles in water. Gold particles dispersed in water are negatively charged due to their ionic characteristics of gold micelles. The repulsive electrostatic forces between gold nanoparticles protect them against agglomeration and sedimentation in the water suspension.

Fig. 7 shows typical the UV–Vis absorption spectra for the gold nanoparticles suspension. The maximum absorbance at around 525 nm can be also found in other papers [5–7].

During gold nanoparticles production by arc discharge in water we also can observe water decomposition (electrolysis). As a result gaseous hydrogen and oxygen appear in the water as small bubbles partly dissolved in the water. Hydrogen and oxygen start to interact with the newly prepared gold nanoparticles. Since hydrogen (molecular or atomic form) does not adsorb on a gold surface at room temperature [8–10], it is ultimately removed from the water suspension to the gas phase. However oxygen can be adsorbed on a gold surface at room temperature [11–13]. Based on our results and observation we suppose that negatively charged surface of gold nanoparticles (electrons are injected into the gold nanoparticles by the cathode during arc discharge) are saturated by atomic oxygen, which

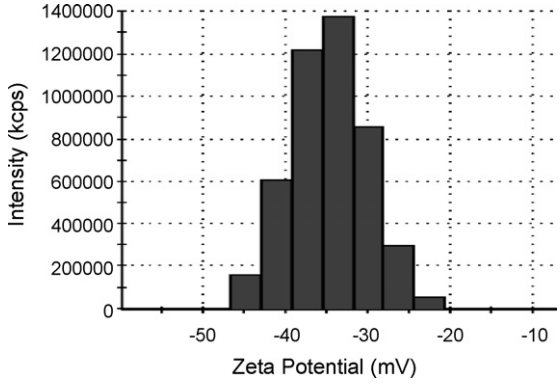

Fig. 6. Zeta potential of the aqueous gold colloid.

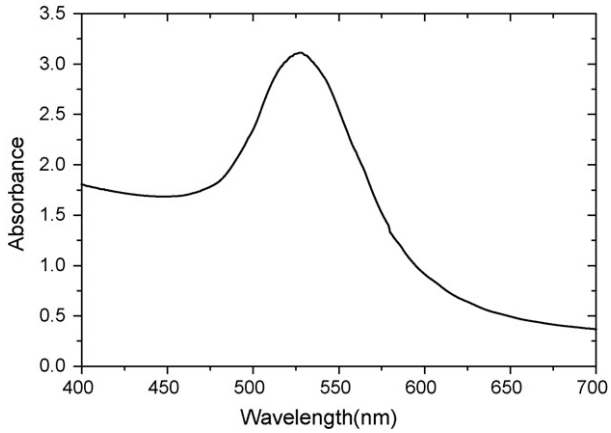

Fig. 7. UV–Vis absorption spectra of the aqueous gold colloid.

can create hydrogen bonds with water particles in a water environment. Finally, negatively charged gold nanoparticle micelles are created in the water medium. Fig. 8 presents model of the gold nanoparticle micelles formation. Due to hydrogen bonding, marked here by a dash line, water molecules are bonded with the gold nanoparticles. Without any stabilizers and surfactants, negatively charged gold nanoparticles surrounded by water molecules can create a stable suspension. Such a gold colloid can be heated up to 100 °C without destruction of its structure.

The simple and cheap DC arc discharge process can ensure high reproducibility of the production of similar-size of Au nanoparticles. This method is promising as an alternative to other methods for nanoparticles preparation. DC arc discharge in water provides an effective and rapid mass-production method for gold nanoparticles preparation without any surfactants or stabilizers.

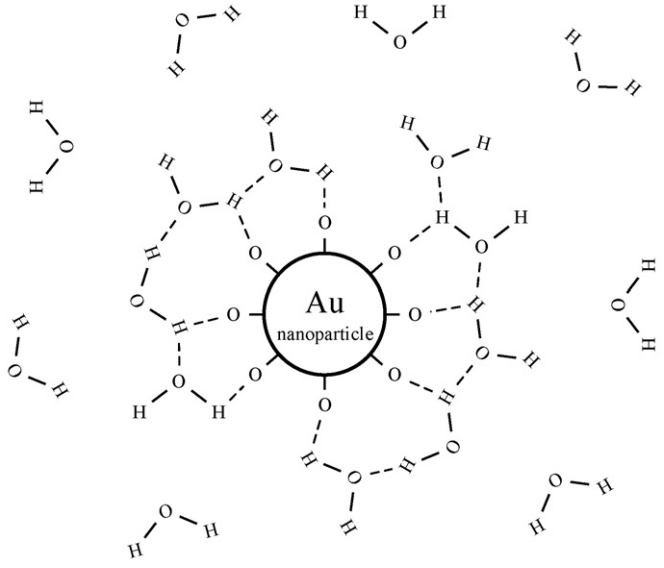

Fig. 8. Model of the gold nanoparticle micelle suspended in water. Due to hydrogen bonding marked here by (- - -), water molecules are bonded with the gold nanoparticles.

4. Conclusions

1. The DC arc discharge in water method has been successfully developed for gold nanoparticles production.
2. Gold nanoparticles in water without any surfactants or stabilizers are characterized as a stable colloid, which can be stored in a glass container for a fairly long time at room temperature without visible sedimentation.
3. DC arc discharge in water is a cheap, effective, rapid and environmental friendly process for gold nanoparticles production. This process can be applied in future as a method for mass production of nano-sized gold nanoparticles.
4. Future studies on voltage, current, time and temperature dependences, electric double layer will be continued to better understand the mechanism of formation of Au nanoparticles and their stability in a water medium.

Acknowledgment

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