SONOELECTROCHEMICAL SYNTHESIS OF MONOMETALLIC AND BIMETALLIC NANOPARTICLES

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ABSTRACT

Noble monometallic and bimetallic nanoparticles have a wide spectrum of applications such as catalysis, sensors, microcontrollers etc. There are many different methods that are used in order to create/synthesize nanoparticles. In this work we demonstrate the synthesis of monometallic and bimetallic nanoparticles via pulsed sonoelectrochemistry. Specifically, such nanoparticles have been synthesized using pulsed current and/or pulsed sonication. Current density defines the shape and size of the nanoparticles that are created while the sonication time enhances the dispersion and the mass transport of the nanoparticles. An ultrasound emitter is used which is connected with the electrochemical cell and is considered the cathode (sonotrode). This method applies to different kinds of solutions which have dissolved metal salts or even solutions with dissolved bulk substrates of the desirable metal/metals. The solutions may also have some stabilizers in order to control the dispersion and avoid the agglomeration of the nanoparticles. The parameters that affect the quality and the quantity of the created nanoparticles are the temperature of the experiment, the current density that is applied, the sonication time and the concentration of the stabilizers. In this work the synthesis of monometallic Ag, Au and bimetallic Ag/Au nanoparticles is presented.

INTRODUCTION

Over the years have been synthesized metallic nanoparticles with different methods like thermal decomposition, physical and thermal evaporation, laser ablation, chemical oxidation and sol-gel methods [1-3]. Nevertheless most of these methods are considered both cost and time consuming. Sonoelectrochemistry on the other hand is a very cost and time effective technique which provides a great variety of nanoparticles and nanostructures while combines the principles of metal electrodeposition in which

$$M^{n+}_{(aq)} + ne^- \rightarrow M_{(electrode)} \qquad (1)$$

a metal will be deposited on the cathode when the potential and the electrolyte are suitable for the above transition (1) and the cavitation effect in which the ultrasound creates hot spot of negative pressure states in which bubbles are created grow and then collapse. When the bubbles collapse spots with high temperature (~5000K) and pressure are generated [4-6]. A great variety of nanoparticles and nanostructures have been synthesized via sonoelectrochemistry and sonochemistry. More specifically Cu, Pt, Mg, Al, Pd, Se, Ag, Au nanoparticles have been reported as well as binary nanopowders like CoFe, FeCr and core-shell Cu-Ag[7-10].

EXPERIMENTAL SECTION

All chemicals ($(HAuCl_4 \cdot 3H_2O$ (≥49%), $AgNO_3$ (≥99.8%), Nitric acid (≥65%), Polyvinylpyrrolidone (PVP)) were used without further purification. All solutions were prepared using distilled water.

The experiments have been conducted to a three electrode cell where an ultrasound emitter acted as the cathode (sonotrode),a Pt wire was used as the anode and as a reference electrode was used an Ag/AgCl saturated electrode. The arrangement was controlled by the potensiostat (Biologic SP-150).

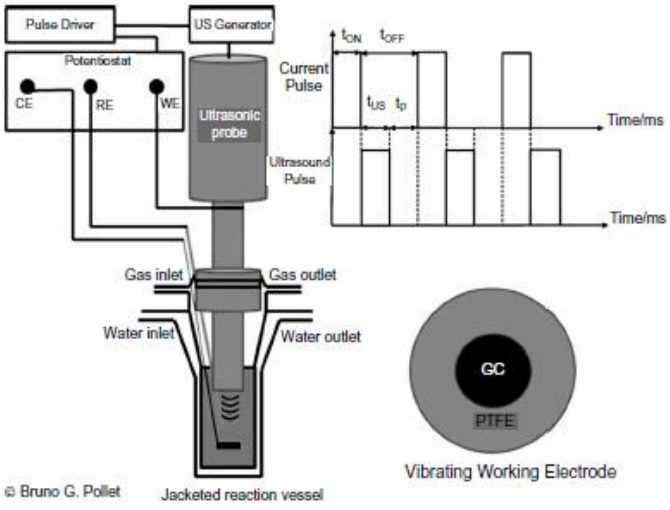

Figure 1. *Sonoelectrochemistry arrangement (© Bruno G.Pollet).*

The ultrasound emitter (sonotrode Sonics Vibracell VCX 750W) with a surface area of 1.27 cm^2 was immerged directly into the solution. All experiments were conducted under controlled temperature bath with continuous nitrogen gas flow. The experiments that were conducted can be divided into 2 groups:

1. Continuous sonication and current.

These experiments were conducted using simultaneously sonication and potential difference.

2. Pulsed sonication and current

These experiments were conducted using pulsed sonication and current most commonly known in the bibliography as an out-of-phase ultrasound.

It is worth mentioning that the duration of the pulses were calculated by the time-management equation (2)

$X=T_{on}/T_{off}+T_{us}$ when $0.3 \leq X \leq 0.5$ (2)

where T_{on} is the duration of the current/potential pulse, T_{off} is the duration of the pulse where neither potential nor ultrasound is triggered and T_{us} is the duration of the pulse where the ultrasound is active.

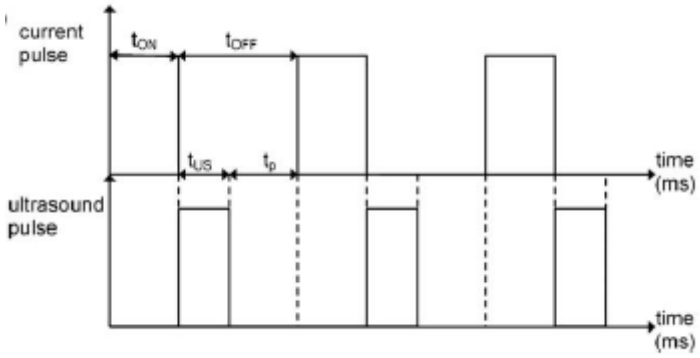

Figure 2. *Presentation of time sequence of the pulses.*

Synthesis of Au monometallic nanoparticles

10mM of $HAuCl_4$ where dissolved in 100ml water with 20 g/l concentration of PVP. Then the pH was adjusted to 1 using HNO_3. The temperature of the bath was held at 299 K while nitrogen was flowing into the electrochemical cell during the experiment.

Synthesis of Ag monometallic nanoparticles

10mM of $AgNO_3$ where dissolved in 100 ml water with 20 g/l concentration of PVP. Then the pH was adjusted to 2 using HNO_3. The temperature of the bath was held at 299 K while nitrogen was flowing into the electrochemical cell during the experiment.

Synthesis of Au/Ag bimetallic nanostructure

10mM of $HAuCl_4$ and 10mM of $AgNO_3$ where dissolved in 100ml water with 20 g/l concentration of PVP. Then the pH was adjusted to 1 using HNO_3. The temperature of the bath was held at 299 K while nitrogen was flowing into the electrochemical cell during the experiment.

RESULTS AND DISCUSSION

Cyclic Voltametry of Au solution

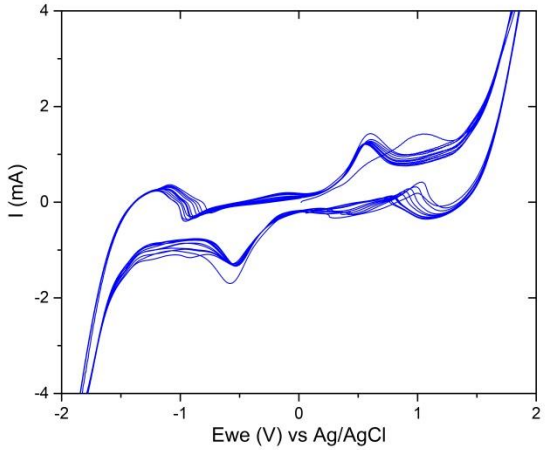

Figure 3. *Cyclic Voltametry of Au solution.*

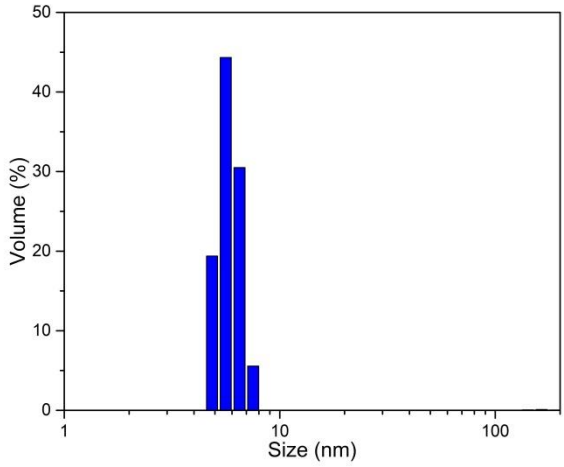

Figure 4. *DLS results of Au nanoparticles.*

Based on the reduction peak of the sample the suitable reduction potential has been selected (E=1.49V). The arrangement was set to potentiostatic mode for 30 min with constant ultrasound emulsions. The produced solution was analysed with DLS resulting a mean size of 5.8nm of Au nanoparticles.

Cyclic Voltametry of Ag solution

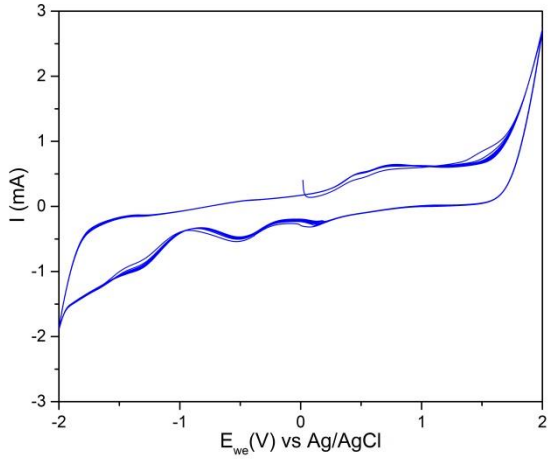

Figure 5. *Cyclic Voltagram of Ag solution.*

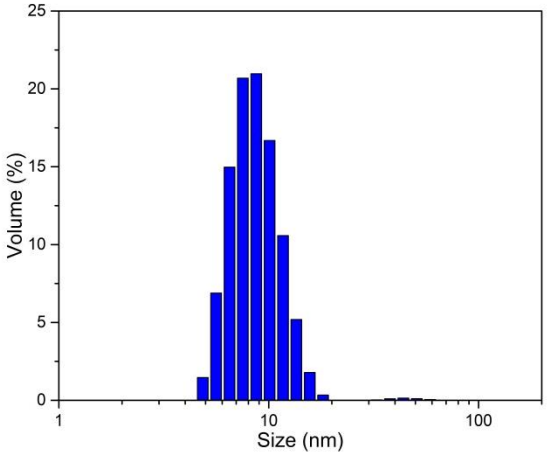

Figure 6. *DLS results Ag nanoparticles.*

Based on the reduction peak of the sample the suitable reduction potential has been selected (E=0.75V). The arrangement was set to potentiostatic mode for 30 min with constant ultrasound emulsions. The produced solution was analysed with DLS resulting a mean size of 7.3nm of Ag nanoparticles.

Cyclic Voltametry of bimetallic Au/Ag solution

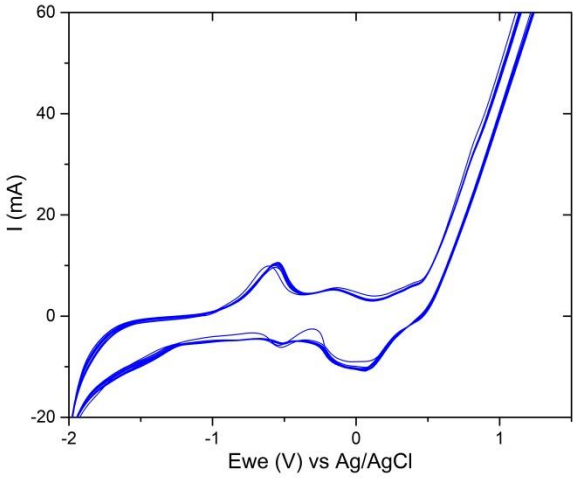

Figure 7. *Cyclic Voltagram of Au/Ag solution.*

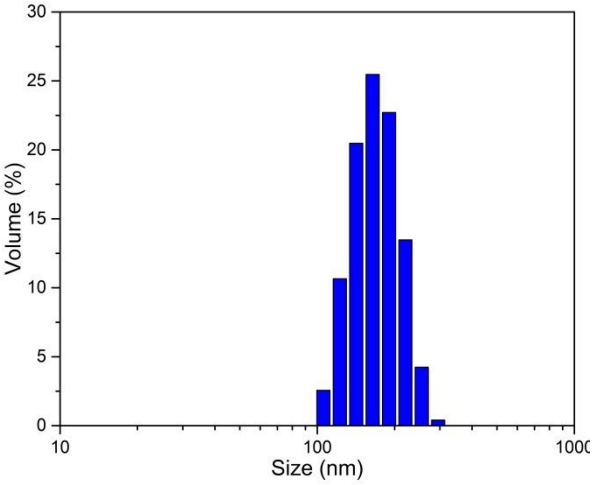

Figure 8. *DLS results of Au/Ag nanostructure.*

Based on the reduction peaks of the sample different reduction potentials have been selected. The most promising results were obtained by the pulsed technique in which a potential (E=1.46V) was set for 100ms followed by an ultrasound pulse for 100ms followed by a relaxation time duration of 200ms. The produced solution was analysed with DLS resulting a mean size of 171nm Au-Ag nanostructure.

CONCLUSIONS

Monometallic and bimetallic nanoparticles have been produced via sonoelectrochemistry by using PVP as a stabilizer. The results revealed that bimetallic nanoparticles have an increased mean size. The research is now focused in the ability of creating binary or multi-metals in the nanoscale creating different nanostructures and shapes by sonoelectrochemical technique. More research is required in order to understand the possibilities and the restrictions of this method.

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