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Copper Electrocrystallization on Titanium Electrodes: Controlled Growth of Copper Nuclei Using a Potential Step Technique

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Abstract

Copper nanoparticles were synthesized using a pulsed sonoelectrochemical (20 kHz, 78 Wcm^{-2}) method. Two electrolytes used were a copper salt dissolved in Na_2SO_4 (pH=3.80) or H_2SO_4 (pH=0.6). For both electrolytes and in the absence of any surfactant, monodispersed spherical copper nanoparticles were strongly aggregated in three-dimensional clusters of about 200nm. The particle size is controlled by varying reaction parameters such as duration of the experiment, current density, temperature and ultrasound power. A potential step technique is proposed to synthesize copper nanoparticules. Under potentiostatic conditions the aim is to control and decrease the nanoparticle size and reduce production costs by avoiding gas evolution and other adverse reactions.

Keywords: copper; electrochemistry; nanoparticle; sonochemical

1. Introduction

Nowadays nanoparticles have broad applications in a variety of fields because of their unusual and size dependent optical, magnetic, electronic and chemical properties. The nanoparticles are characterized by an extremely large surface to volume ratio, and their properties are determined mainly by the behaviour of their surface. The application of nanoparticles is well known in the fields of cosmetics and pharmaceutical products, coatings, electronics, polishing, semiconductors and catalysis.

Copper nanoparticles have been applied in the preparation of conductive adhesives and conductive coating systems; moreover these nanoparticles can be used as pigments in ink-jet inks. The price of precious metals, such as Au and Pd, has increased rapidly, and so more attention is being paid to more inexpensive metals such as copper. The synthesis of copper nanoparticles has not been as widely explored due to the easily oxidized nature of copper caused by the relatively low Cu^0/Cu^{2+} redox potential (+0.34V). Moreover, copper nanoparticles are instable with

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tendency to agglomerate in the absence of some surfactant. In spite of this, some methods have been reported in the literature to prepare copper nanoparticles such as radiation methods [1], thermal decomposition [2], vapor deposition [3], reduction in microemulsions [4] and chemical reduction methods [5]. Recent work [6,7] has developed a new technology for the production of nanoparticles, which combines pulsed electrochemistry and pulsed ultrasound. In these experiments the sonotrode acts as both an ultrasound emitter and a cathode. First, a pulse of electric current is applied to produce a high density of fine metal nuclei followed by a short pulse of ultrasonic energy in order to remove the metal particles from the cathode. The ultrasonic pulse cleans the surface of the cathode, and replenishes the double layer with metal cations by stirring the solution [7]. Some advantages of this method are its low cost, safety, environmental friendliness, and versatility, as well as the use of water as a solvent. In this case, nanoparticle production process depends upon electrochemistry and ultrasonic variables, such as current density, current pulse time, ultrasonic power, ultrasonic pulse besides pH, temperature and bath composition (presence of surfactants). The size and shape of the nanoparticles will depend of the control of these variables in the process.

The aim of this work is to obtain copper nanoparticles by pulsed sonoelectrochemistry with a narrow particle size distribution. In our laboratory, first experiments were carried out under galvanostatic deposition conditions, initially a current density of 50 mA cm^{-2} was applied during 250 ms followed by an ultrasonic pulse, 78 W cm^{-2}, for 250 ms. In our experimental conditions, with different electrolytes and surfactants, the nanoparticle size was always higher than 200 nm and moreover a wide particle size distribution was observed. Previous work [] has suggested high current densities are necessary to decrease nanoparticle size, but higher current densities decrease the process yield and the majority of the current is used to evolve hydrogen. Under potentiostatic conditions the aim is to control and decrease the nanoparticle size and reduce production costs by avoiding gas evolution and other adverse reactions.

2. Experimental

2.1. Electrochemical experiments

Chronoamperommetry experiments were carried out using a Voltalab 40 (model PGZ301, Radiometer Analytical, Lyon, France). The electrochemical cell consisted of a conventional three-electrode configuration using a titanium RDE (0.07 cm^2) as the working, platinum plate (1 cm^2) as counter and saturated calomel (SCE) as reference electrodes.

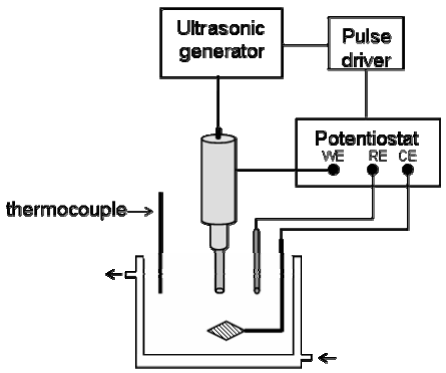

Fig.1 Sketch of the sonoelectrochemical equipment. WE = working electrode; RE = reference electrode; CE = counter electrode

2.2. Sonoelectrochemical experiments

The sonoelectrochemical device used for the production of nanoparticles has been described elsewhere [, 8]. The system consisted of a titanium alloy horn (Ultrasound generator Sonics Vibracell VCX 600, 20 kHz) acting both as the cathode and the ultrasound emitter (Figure 1). A constant current was applied to the sonoelectrode during a short period of time followed by a short pulse of ultrasonic energy.

In this study, the ultrasound power was determined by the calorimetric method as described in [9].

All experiments were carried out at an ultrasound intensity of 78 W cm^{-2}.

3. Results

3.1. Synthesis of copper nanoparticles produced by pulsed sonoelectrochemistry

Under galvanostatic deposition conditions a set of experiments were carried out. In these experiments, current densities were applied in the range from 50 to 200 mA cm^{-2} for 250 ms followed by an ultrasonic pulse, 78 W cm^{-2}, for 250 ms. The electrolytes used were a copper salt dissolved in Na_2SO_4 (pH=3.80) or H_2SO_4 (pH=0.6), in some cases PVP was used as a surfactant. Figure 2 shows the UV-vis absorption spectrum of copper nanoparticles, an absorption band at 570 nm can be observed, which is due to the surface plasmon bands for the copper nanoparticles [10]. For our experimental conditions, the nanoparticles size was always higher than 200 nm and moreover a wide particle size distribution was observed.

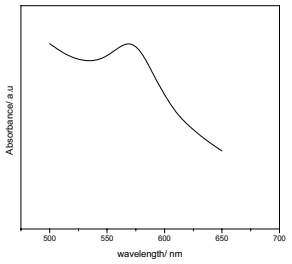

Fig.2 UV-vis absorption spectrum of copper nanoparticles. 30 g L^{-1} $CuSO_4$ $5H_2O$ + 0.05M Na_2SO_4 1% PVP , 200mA cm^{-2} 250 mS, 78 W cm^{-2} US 250 mS.

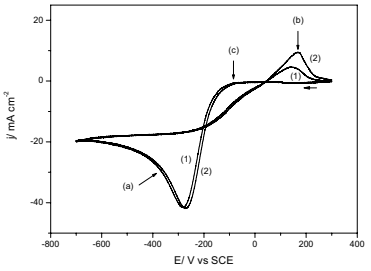

Fig.3 Cyclic voltammograms for copper electrodeposition on titanium from 30 g L^{-1} $CuSO_4$ $5H_2O$ + 150 g L^{-1} H_2SO_4, scan rate 20 mV s^{-1}.

3.2. Study of copper electrocrystallization

Figure 3 shows typical cyclic voltammogram for copper electrodeposition on titanium electrode from 30 g L^{-1} $CuSO_4$ $5H_2O$ + 150 g L^{-1} H_2SO_4 solution. From this figure it can be observed that the metal started to deposit at potential lower than -200 mV vs SCE on the negative potential sweep, and from that, there is an increase in the cathodic current, due to the copper crystallization. Cathodic current increased quickly at potential more negative to -750 mV vs SCE, showing that hydrogen evolution reaction was taking place (curve not shown). On the reverse scan the anodic stripping peak due to the dissolution of copper was observed at a potential of 160 mV vs SCE. In this work a set of step potential experiments have been proposed to produce metal nanoparticles of a small size.

Figure 4 shows the step potential applied and the deposition time. During the first stage (a in the cyclic voltammogram, see figure 1) nuclei of copper with a supercritical size were formed, after that, stripping peak

potential was applied (b in the cyclic voltammogram) to remove smaller metal nuclei partly, and at last a potential was applied where the nuclei could grow slowly (c in the cyclic voltammogram). It is important to note that from figure 3 no copper deposition was observed on a fresh titanium surface at -100mV vs SCE, this means that possible new nuclei of copper were not formed at titanium electrode surface at this potential. With the aid of a stepped potential experiment, it has been possible to synthesize copper nanoparticles and obtain a reduction of the mean diameter of these nanoparticles. The mean diameter observed was 81 nm and the standard deviation of the size distributions was 5. Figure 5 shows a SEM image of copper clusters on titanium electrode obtained under the potentiostatic conditions shown in figure 4. It is important to emphasize that these experiments were carried out without any stabiliser in the solution.

Further work is in progress in order to study the effect of the surfactants.

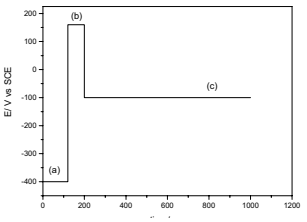

Fig.4 Variation of the electrode potential versus time in the potential step experiments.

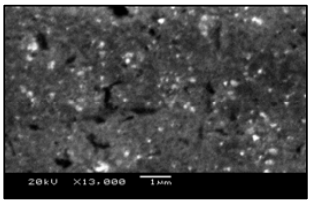

Fig.5 SEM image of copper clusters obtained under potentiostatic conditions from 30 g L-1 CuSO4 5H2O + 150 g L-1 H2SO4. Ea= -400 mV 120 mS, Eb= 160 mV 80 mS and Ec=-100 mV 7s.

4. Conclusions

The sonolectrochemical production of nanoparticules was carried out using a potential step technique. Under potentiostatic conditions the aim is to control and decrease the nanoparticle size and reduce production costs by avoiding gas evolution and other adverse reactions. The mean diameter observed was 81 nm and the standard deviation of the size distributions was 5.

Acknowledgments

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