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Synthesis of spherical copper-platinum nanoparticles by sonoelectrochemistry followed by conversion reaction

Samuel Levi[a], Valérie Mancier[a], Céline Rousse[a], Omar Lozano Garcia[b], Jorge Mejia[b], Maribel Guzman[c], Stéphane Lucas[b], Patrick Fricoteaux[a,*]

[a] LISM, EA 4695, UFR Sciences Exactes et Naturelles, BP 1039, F-51687 Reims Cedex 2, France
[b] Namur Nanosafety Center (NNC), NAmur Research Institute for LIfe Sciences (NARILIS), Research Centre for the Physics of Matter and Radiation (PMR), University of Namur (UNamur), rue de Bruxelles 61, B-5000 Namur, Belgium
[c] PUCP, Engineering Department, Av. Universitaria 1801, Lima-32, Peru

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ABSTRACT

Cu-Pt nanopowders were prepared by sonoelectrochemistry followed by a displacement reaction. The first method provides pure copper particles. In the second method the surface copper atoms are replaced by platinum atoms. The influence of dissolved oxygen during the conversion reaction was also studied. Nanoparticles (NPs) were observed by transmission electron microscopy (TEM) and their size distribution was determined by centrifugal liquid sedimentation (CLS). The mean diameter of isolated particles was found to be around 8 nm. Their composition was studied by energy dispersive X-ray spectroscopy (EDXS) and X-Ray photoelectron spectrometry (XPS). These analyses and X-ray diffraction (XRD) patterns showed that the particle shell is a solid solution of Cu and Pt. The shell composition is heterogeneous with a richer Pt percentage on its surface.

1. Introduction

Over the last two decades the interest for nanotechnology has increased markedly. This interest for nanoparticles can be explained by their various fields of application. Among them, medicine (cancer therapy [1,2], IRM contrasting agent [3] or drug delivering [4]), sensors [5], energy storage [6] and catalysis [7,8] can be cited. Nanoparticles are characterized by a high surface-to-volume ratio. As the properties of a material mainly depend on its surface, nanoparticles synthesis is an interesting way to enhance the materials characteristics.

Nowadays a large range of nanoparticles production methods are available: chemical or physical vapor deposition (CVD [9] and PVD [10]), laser ablation [11], sol-gel and solvothermal synthesis [12], reduction in emulsion [13,14] and thermal decomposition [15]. Other simple ways of producing nanoparticles are classical electrochemistry - under pulsed current [16] or not [17] - and sonoelectrochemistry.

High intensity ultrasounds have been used in chemistry [18] since 1934 and are still used now to synthesize advanced materials such as nanomaterials and nanoalloys [19,20]. The combination of electrodeposition and ultrasound was first employed around 1950 [21]. The major effect of ultrasound propagation in an aqueous solution is acoustic cavitation i.e. formation, growth and collapse of microbubbles. During the negative pressure phase, bubbles are formed and grow to a size of 5 to 20 μm [22]. During the compression cycle, these bubbles rapidly collapse, local temperature rises to a thousand kelvin and pressure to hundreds of bars. Strong shock waves and very high cooling rate can also be observed around the bubbles. When they collapse a liquid jet forms. If the cavitation takes place nearby, the jet erodes the surface. Other physical and chemical effects have been observed such as: mass transport improvement, diffusion layer decrease, cleaning and degreasing of the electrode surface and formation of radicals like $OH^{\bullet}$ [23–25]. Several sonoelectrochemical setups were elaborated. The first one used a classical electrochemical cell dipped into an ultrasound bath with the power transmitted to the electrochemical cell varying according to the spatial configuration of the setup [26]. Next, another configuration was developed in which the cathode (working electrode) is coupled to the transducers; this new electrode was named sonotrode [27]. With this specific device, Reisse et al. [28] studied copper electrodeposition and showed the interest of ultrasound to produce copper nanopowders. This setup was later used to produce various nanoparticles such as: pure metals (Zn [29], Ni [29], Pt [30], Au [31], Ag [32]), alloys

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[*] Corresponding author. Tel.: +33 326 91 85 82; fax: +33 326 91 89 15.
E-mail address: patrick.fricoteaux@univ-reims.fr (P. Fricoteaux).

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[33,34], oxides [35] and core-shell structures (a material covered by another material) [36].

At nanometric scale, platinum (catalytic material) has been extensively studied because the nanostructures enhance the active surface. Usual applications are electrocatalyst for oxygen reduction reaction in fuel cells [37], cyclopropanation [38], cycloisomerization [39] or Suzuki coupling [40]. Displacement of platinum ions on bulk copper can be employed to lead Pt deposition [41], a very convenient way to deposit a noble metal. In 2010, Sarkar and Manthiran achieved synthesis of Cu-Pt NPs using a chemical reduction to synthesize the copper core and a displacement reaction to create the platinum shell [42]. Those nanostructures have several interests. Firstly, core-shell nanostructures may combine the properties of the two metallic components [43,44]. Secondly, in the case of expensive material (as platinum) the use of a less expensive material as a core decreases the production cost for a same active surface.

Moreover it has been shown that Cu-Pt NPs are four times more efficient as a catalyst for the oxygen reduction reaction than pure Pt NPs [45].

For this paper, the researches were conducted in order to define new parameters for the synthesis of Cu-Pt NPs combining sonoelectrochemistry and galvanic displacement.

2. Experimental section

2.1. Electrolytic solutions

The solution for copper electrolysis was made with copper sulfate pentahydrate ($CuSO_4$, $5H_2O$) at 0.2 mol.L^{-1} and sulfuric acid (H_2SO_4) at 0.9 mol.L^{-1}. The platinum bath was a mixture of Na_2PtCl_6 (0.001 mol.L^{-1}) and sulfuric acid (0.45 mol.L^{-1}). Copper sulfate was bought from Panreac, sulfuric acid and platinum salt were bought from Chimie Plus Laboratoires. The three reagents were used without any further purification. The copper electrolyte was regulated at 30 °C. The conversion of platinum was done at ambient temperature.

2.2. Preliminary study

In order to synthesize copper nanoparticles, the reduction potential of the copper was determined by recording a current density versus potential curve. A disc of titanium ($S = 0.785$ cm^2) was used as working electrode and a copper wire as soluble counter electrode. The reference electrode was a mercury saturated sulfate electrode noted SSE (0.64 V vs SHE). The potentiostat employed was a home-made one. The current density versus potential curve presented in Fig. 1 was recorded with a scan rate of 20 mV.s^{-1}. In the cathodic part of the curve, the reduction of copper appeared at −600 mV vs SSE (Eq. (1)) while the hydrogen evolution (Eq. (2)) happened around −1200 mV vs SSE. Since the hydrogen evolution is an adverse reaction, the electrolysis potential has to be set between −600 and −1200 mV vs SSE. The potential of −1000 mV vs SSE was arbitrarily chosen to carry out the production of copper nanoparticles.

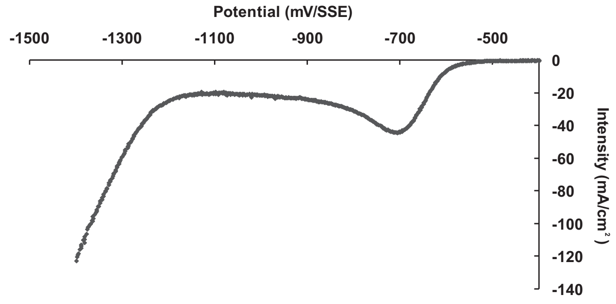

Fig. 1. Current density-potentiel curve for Cu(II) solution reduction at T = 30 °C. Scanning rate = 20 mV.s^{-1}.

$$Cu^{2+} + 2\,e^- \rightarrow Cu \qquad (1)$$

$$2\,H^+ + 2\,e^- \rightarrow H_2 \qquad (2)$$

2.3. Copper nanoparticles synthesis

Copper nanoparticles were produced using out-of-phase pulsed sonoelectrochemical setup (Fig 2a). Two generators are necessary. A potentiostat, connected to the working electrode of the sonotrode, manages electrolysis. An ultrasonic generator connected to tranducers, placed at the top of the sonotrode, allows their vibrations. The latter induce surface working electrode vibrations that pull off the electrodeposit. These two systems are independant and never work at the same time. A rest time is also applied between ultrasounds generation and electrolysis in order to reduce acoustic streaming in solution, diffusion layer and possible electronic interactions. This setup, patented by Winand et al. [28,46], has been widely and successfully employed to produce numerous powders. In this work, the previous home-made potentiostat was linked via a trigger to a titanium sonotrode (Linea S23-10-1/2 manufactered by Sinaptec) powered by a Nexus P198-R generator (Sinaptec). The sonotrode was supplied with an electrical current set at a frequency around 24 kHz. To avoid overheating, the piezoelectric transducers were cooled with compressed air. The Cu NPs synthesis was controlled using a classical three electrode electrochemical setup. The reference electrode was the SSE, the soluble counter electrode was made with a copper wire and the working electrode was the sonotrode. The side parts of the sonotrode were insulated with a sleeve to let only a planar circular surface at the bottom of the horn as electroactive surface (0.785 cm^2). Since high intensity ultrasounds can damage the sintered material, the reference electrode was placed in a second beaker filled with saturated potassium sulfate K_2SO_4. The link between the beaker and the electrochemical cell was a bridge filled with the copper electrolyte. The counter electrode was covered with a polyethylene net to avoid mixing of the copper particles coming from the counter electrode ultrasonic erosion with the copper nanoparticles produced by electrolysis.

Before experiments, the oxygen was removed from electrolyte by nitrogen bubbling during 20 minutes. During electrolysis, the nitrogen bubbling was stopped to avoid the change of the ultrasonic waves frequency and because a sonicated solution is de facto degassed. In order to produce Cu NPs, a pulse of polarization (−1000 mV vs SSE; pulse duration = 100 ms) was applied which produces nuclei at the surface of the sonotrode. Those nuclei were immediately pulled off the surface using a 100 W.cm^{-2} power ultrasonic pulse for 100 milliseconds. Applied potential for electrolysis and ultrasound pulses were used out of phase, without any latency between them. Then a free time of 100 ms was applied to let the diffusion of electrochemical species. The sequence of these pulses was repeated to produce large amounts of Cu NPs (Fig. 2b).

After the sonoelectrochemical synthesis, the copper nanoparticles suspension was filtered under vacuum using a hydrophilic polyethersulfone membrane (Sartorius Biolab Products 15458) before several washings in large volumes of deionized water and with deoxygenated ethanol. Powders were removed from the filter by immersion in degassed ethanol and sonication in an ultrasonic tank. The obtained copper nanopowders were dried after sedimentation and placed under vacuum to avoid oxidation.