Sonoelectrochemical (20 kHz) production of platinum nanoparticles from aqueous solutions

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ABSTRACT

The present work describes the production of platinum nanoparticles from aqueous chloroplatinic solutions in the presence of low-frequency high-power ultrasound (20 kHz) on titanium alloy electrodes. The production of this new type of Pt nanoparticles was performed galvanostatically at (298 ± 1) K using a newly designed experimental set-up and '*sonoelectrode*' producing ultrasonic pulses triggered and followed immediately by short applied current pulses. From galvanostatic studies, it was shown that Pt mean grain size ranging from 11 to 15 nm was produced. Morphological and structural studies of the produced nanoparticles were performed by TEM, SEM, XRD and SAED and showed that Pt nanoaggregates were predominantly formed, with no redissolution of the nanoaggregates. Globular clusters had a mean size ranging between 100 and 200 nm which in turn aggregated and built complex structures.

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1. Introduction

The use of ultrasound on electrochemical systems or Sonoelectrochemistry was first observed by Moriguchi as early as 1934 [1] and continues to be an active and exciting research area [2]. Extensive work has been carried out in which high power ultrasound was applied to various electrochemical processes leading to several industrial applications and many publications over a wide range of subject areas such as electrodeposition, electroplating, electrochemical dissolution and corrosion testing.

It was shown that the effects of high intensity ultrasonic irradiation on electrochemical processes lead to both chemical and physical effects, for example, mass-transport enhancement, surface cleaning and radical formation. Many workers have also investigated the distribution of ultrasonic waves or energy in various electrochemical reactors operating in the lower ultrasonic frequency range (20–100 kHz) and at high ultrasonic powers. Several methods for such determination have been proposed, e.g. aluminum foil erosion, sonoluminescence, calorimetric methods, chemical dosimetry [2] and laser-sheet visualization [3].

Many of the observed effects in Sonoelectrochemistry may be explained by the enhancement of mass-transport in diffusion-controlled processes. The extensive work of Coury and co-worker [4] and Compton et al. [5,6] were probably the first "modern"

examples investigating mass transfer phenomena under sonication. Power ultrasound is known to decrease the diffusion layer thickness (δ) thereby giving substantial increase in limiting current ($I_{\lim}$) attributed due to effects of cavitation and/or micro- and macro-streaming. It is known in the field that both cavitational and acoustic streaming effects contribute significantly to the increase in observed experimental currents [4–7]. The experimental decrease in the diffusion layer thickness is also known to be due to asymmetrical collapse of cavitation bubbles at the electrode surface leading to the formation of high velocity jets of liquid being directed toward its surface. This jetting, together with acoustic streaming, is thought to lead to random punctuation and disruption of the mass transfer boundary layer at the electrode surface at close electrode-to-horn separations. Birkin et al. [8,9] also showed that the nature of the solvent is paramount in assigning limiting currents. More recently, Pollet et al. [10] showed, with aid of mathematical models based on mass-balance equations, that a Levich-like equation relating the limiting current density, the square root of ultrasonic intensity and the inverse square root of the electrode–horn distance, may be generated for ultrasonic frequencies of 20 and 40 kHz allowing the generation of an 'equivalent' flow velocity under sonication, an important and useful parameter in chemical engineering.

Recently, an upsurge of interests has been observed in the synthesis of metallic nanoparticles [11–13]. In the last decade, the production of metallic platinum nanoparticles has been investigated as they offer high surface-to-volume ratios and have considerable potential for usage in various areas such as fuel cells, reforming, catalysis and medicine [14,15]. There are a range

of methods of producing metallic platinum nanosized materials including thermal decomposition, physical and thermal evaporation, laser ablation, laser-assisted catalytic growth (LCG), vapor–liquid–solid growth (VLS), ultrahigh-vacuum (UHV), ion implantation, biochemical, electrochemical, sonochemical, radiolysis, chemical reduction/oxidation and sol–gel [15]. However, most of these techniques tend to be expensive and time-consuming. An alternative method, which is both simple and cost-effective, is the use of Sonoelectrochemistry. For example, based on the original work of Reisse et al. [16,17] for the production of copper, Dabalà and Pollet [18] produced for the first time nanosized Fe–Co metallic particles sonoelectrochemically, in which the ultrasonic horn was used as the working electrode. This 'sonoelectrode' was subjected to ultrasonic pulses which were each followed by short applied current pulses. They showed that, during cavitation, a jet of liquid penetrates inside the cavitation bubble perpendicular to the 'sonoelectrode' surface and the resulting impact was responsible for dislodging any nanopowder material which had been electrochemically deposited on the surface.

This paper reports for the first time, a study on the synthesis of platinum nanoparticles by using the new method combining metallic electrodeposition with low-frequency high-power ultrasound (20 kHz). In this study the platinum nanopowders produced were characterized both morphologically and chemically.

2. Experimental

The apparatus employed for the production of platinum nanosized materials was similar to that employed by Reisse et al. and Pollet and Dabalà [17,18] [Fig. 1(a)]. The system consisted of a two-electrode set-up, namely (i) a titanium alloy (Ti–6Al–4V) horn acting both as the cathode and the ultrasonic emitter (described therein as the sonoelectrode) linked to a AMEL 7060 potentiostat

operating in galvanostatic mode and a 20 kHz ultrasonic generator (Sintec Generator EG36) and (ii) a platinum mesh acting as the anode linked to the potentiostat. Electrochemical experiments were performed using a cylindrical vessel (200 ml) [Fig. 1(a)]. The electrochemical cell was placed in a Faraday cage. Temperature was regulated by a glass cooling coil (C) placed inside the electrochemical cell and linked to a thermostatted bath operating at preset temperatures. The temperature of the electro-analyte was measured with a Fluke 51 digital thermometer fitted to a K-type thermocouple. A heat-shrinkable sleeve surrounded the side walls of the extreme part of the sonoelectrode, leaving only a flat active surface for the electrodeposition equal to 1.227 cm^2 (ultrasonic horn tip area determined coulometrically) [Fig. 1(a)]. A constant galvanostatic current was applied to the sonoelectrode and the maximum ultrasonic power ultrasound employed was 76 W. A trigger acted like a switch with the role of closing alternatively the circuits in which the potentiostat and the piezoelectric power supply operated. The pulse drivers allowed applied galvanic current and ultrasonic pulsing.

All electrodes were electrochemically cleaned by cycling in sulphuric acid (1.0 mol dm^{-3}) for 10 min prior to the experiments. They were then washed with high quality MilliQ water and all Ti electrodes were polished to a mirror finish first with grinding paper (Buelher-Met, P600) and then sequentially with 25 μm down to 0.3 μm alumina oxide paste and were cleaned with immersion in nitric acid for 5 min in order to remove any traces of contaminants.

For the production of nanopowders, the time management sequence employed was as follows [Fig. 1(b)]:

1. A short current pulse of $|i|$ = 50 mA cm^{-2} was applied to the sonoelectrode, and here the titanium horn acted as an electrode only (t_{ON}); the time of this phase typically varied between 0.3 and 0.5 s.
2. Immediately after the electrochemical pulse was turned off, an ultrasonic pulse was sent to the sonoelectrode and here it acted only as a vibrating ultrasonic horn (t_{US}); this second phase lasted no more than 0.5 s.
3. A rest time, t_p, followed the two previous phases (this was useful to restore the initial electrolyte conditions close to the sonoelectrode).

A characteristic time management parameter of the process, χ, was employed according to Eq. (1) [17,18]:

$$\chi = \frac{t_{ON}}{t_{ON} + t_{OFF}} \tag{1}$$

where $t_{OFF} = t_{US} + t_p$

By controlling the varying process parameter, χ, and the applied current, it was possible to produce sonoelectrochemically high purity and high surface/volume ratio suspended nanoparticles which were filtered with 0.05 μm Millipore filters under vacuum.

The filters were then washed with pure ethanol, dried for 48 h in a silica-gel drier and stored under vacuum. Each filter was weighted after dehydration and the efficiency of the process was calculated as the ratio of the produced mass of powder to the faradic yield according to Eq. (2) [19]:

$$m_f = \frac{\chi \cdot I \cdot t}{F} \cdot \frac{\sum_i (x_i \cdot PA_i)}{\sum_i (x_i \cdot n_{ei})} \tag{2}$$

where χ is $t_{ON}/(t_{ON} + t_{OFF})$, I is the applied current in A, t is the total time in s, F is the Faraday constant (96,500 C mol^{-1}), x_i is the molar fraction, PA_i is the atomic weight of Pt in g mol^{-1} (195.09 g mol^{-1}) and n_{ei} is the number of electron transferred (=2).

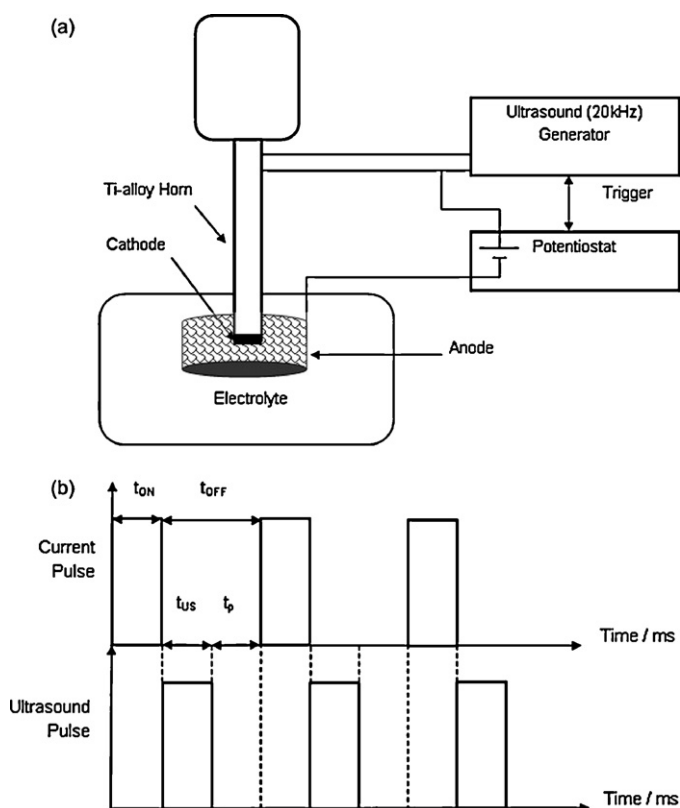**Fig. 1.** (a) Schematic of the sonoelectrochemical nanoparticle production setup and (b) time management for Pt sonoelectrosyntheses.