



# Voltammetric and microscopical investigation of the properties and behaviors of individual mercury micro-droplets



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## ABSTRACT

Mercury film modified electrode based stripping voltammetry has become a rapid and low cost method in routine trace element environmental analysis. However, the understanding of the physical and chemical properties of the plated mercury film still needs to be enhanced till now. It has been recognized that the so-called mercury film actually consists of numerous micro mercury droplets, so it is of significant importance to directly investigate the properties and behaviors associated with the individual droplet. Thus, a platinum ultramicroelectrode was used as the substrate for mercury plating, and only one mercury droplet is formed under this condition. Herein, Fourier Transformed Sinusoidal Voltammetry (FTSV) was employed to investigate both the growth process of a mercury droplet and the behaviors of the droplet after plating. Meanwhile, an optical microscope was used to provide direct visual observation. Investigation suggests that: (a) Both the gradual growth process and the fast coalescence event of individual mercury droplet can be resolved with FTSV; (b) The plated mercury droplet can be partially oxidized immediately after the disconnection between the working electrode and the potentiostat in some circumstances, e.g. the presence of trace amount of chloride ion. The present study not only sheds new light on the properties of mercury film electrode but also demonstrates the feasibility of employing FTSV as a new tool for the characterization of micrometer or even nanometer sized particles.

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## 1. Introduction

Taking advantage of easy fabrication, high stability and less consumption of toxic mercury, electroplating of mercury film on a glassy carbon electrode (GCE) has been widespread use in detection of several kinds of heavy metal ion by anodic stripping voltammetry [1,2]. In mercury electrodeposition process, the surface morphology and nature of mercury thin film significantly affect the results of anodic stripping voltammetry [3,4,6]. To study the mechanisms and properties of mercury film during electroplating process is helpful to control the stability and reproducibility of mercury film electrode, which make great difference to the reproducibility of quantitative analysis.

Previous study has shown that the mercury thin film on an electrode consisted of numerous micro mercury droplets [5,6,7]. It was firstly revealed that mercury droplets would be formed on the relatively active place of a graphite surface then grow up and coalesce with each other [5]. The process of the deposition would be affected by surface morphology [7], deposition time and potential, pH, existence of thiocyanate [8] ion and other complicated factors [9]. Most of the optimal conditions for mercury electroplating were summarized by Fielden [10]. However,

few studies investigated the properties and behaviors associated with single mercury droplet by an electrochemical method. In particular, chronoamperometry is one of the most frequently used techniques for mercury electroplating. However, it shows limits in revealing information with respect to interfacial interaction on an electrode surface, e.g. the mercury droplets coalescence events [11,12]. The so-called current steps or spikes associated with mercury coalescence events were easily misunderstood with the noise and other irrelevant signal. A direct electrochemical characterization method to detect individual mercury droplet has not been reported yet.

Meanwhile, through observation, we found that the plated mercury film would be immediately oxidized as soon as the potentiostatic control was removed. The identical or very relevant phenomena have been reported previously, e.g. Nyholm [13] has indicated that mercury film electrode will lose their surface gradually if they keep immersing in the divalent mercury plating solution. Compton suggested that trace calomel might be formed during mercury electroplating process and it could be reduced on the mercury film electrode with some typical current spikes [14,15]. However, direct voltammetric recording and characterization of the above process has not been realized yet.

At this point, we introduced a new approach to identify and characterize the interfacial interactions between mercury droplets during electroplating process, as well as investigate the oxidation event of mercury film electrode. In this work, we firstly focused our study on plating

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mercury on a platinum ultramicroelectrode (UME) with a diameter of just 10  $\mu\text{m}$ , with the advantage of its high signal to noise ratio and high sensitivity of interface interaction of individual mercury microdroplet [16]. We did not use carbon fiber UME as the substrate for mercury plating mainly because it was difficult for the plated mercury droplet to stably stay on the surface of the UME. The applied potential consisted both direct current (dc) and alternating current (ac) components which enabled us to voltammetrically record and characterize the plating process. The response of mercury film electrodeposition could be analyzed not only in time domain but also in frequency domain. Moreover, the output signals of FTSV could be regarded as a series of vectors which were represented by magnitudes and phase angles [17]. When the heterogeneous interface of mercury droplets coalesced together, the effective surface area of electrode would change so as to cause the change of the current response [11,12,17]. As a consequence, we analyzed the response signal in both time domain and frequency domain to gather information about mercury electroplating process, in order to reveal some properties and behaviors associated with individual mercury droplet. Moreover, FTSV was applied to reveal the mechanism of mercury film oxidation which always happened after the removal of the potentiostatic control. The application of FTSV in this study thus brings a new way to better understand single mercury droplet migration and coalescence in electrodeposition process.

## 2. Experimental section

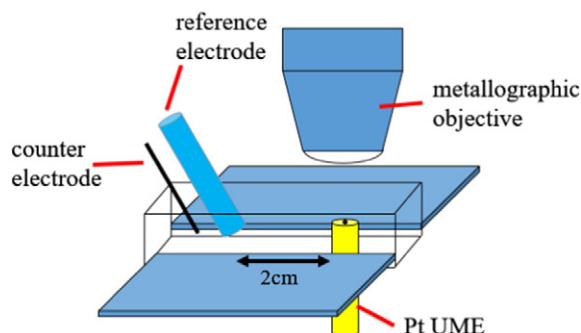
### 2.1. Reagents and chemicals

$\text{Hg}(\text{NO}_3)_2$  (Strem Chemicals, 98%+),  $\text{Hg}_2(\text{NO}_3)_2$  (Aladdin, 98%),  $\text{KNO}_3$  (Fuchen Chemical Reagent, Tianjin, China, 99%),  $\text{HNO}_3$  (Guangzhou Chemical, China, 65.0%–68.0%) were of analytical grade and used without further purification. Deionized water (DI  $\text{H}_2\text{O}$ ) from a Millipore filtration system (PureLab Ultra Genetic, ELGA) having a resistivity of  $18.2 \text{ M}\Omega \cdot \text{cm}$  was used for all experiments.

### 2.2. Apparatus

Sinusoidal voltammetry related experiments were performed with a home-built instrument which consisted of three parts: the compact ultralow current potentiostat (Compact Pico-PStat), the data acquisition card (NI USB6251) and windows based program. The potentiostat, which mainly made up by three operational amplifiers (LMC6002) with the classic adder-type configuration, is very compact and mounted on the inside wall of the Faraday cage. Special cares were taken with respect to guarding and shielding in order to minimize the influence of stray capacitance and interference of line frequency. More details relevant to the instrument can be found in our previous publication [17].

The electrochemical cell used in all our experiment is shown in Scheme 1, where the setup was made by purpose to fit the objective table of the metaloscope. A 10- $\mu\text{m}$ -diameter Pt disk UME working electrode (purchased from Xianren Instrument, Shanghai, China) was



Scheme 1. Schematic illustration of the electrochemical cell used in all our experiments.

inserted in the one side which was under the metallographic objective. A 1-mm Pt wire counter electrode and a fritted saturated calomel reference electrode (SCE) were inserted in the other side far away from the working electrode. The surface of the UME during the whole experiments was in situ observed by a metaloscope (MJ33, Mingmei, China) and recorded with a CCD camera (MC50-N, Mingmei, China). In 3.1 section, the glassy carbon disk electrode with 3 mm diameter (also purchased from Xianren Instrument) was applied to study.

### 2.3. Experimental procedure

The Pt UME was initially polished with polishing films (0.05  $\mu\text{m}$ , NTT-ATADS, Japan), which were widely used for optical fiber polishing. Then the electrode was put into 5%  $\text{HNO}_3$  for 2 min. After rinsed by DI water, a mirror surface could be observed by the metaloscope. The plating solution was injected by an injector connected with the cubic cell and the working electrode was inserted into solution with about 1 mm to make sure platinum surface could be clearly seen with metaloscope. The whole experiment setup including the metaloscope was put in a Faraday cage to avoid any electromagnetic interference. Mercury was deposited onto the Pt UME from a 2.85 mM  $\text{Hg}(\text{NO}_3)_2$  solution with 0.1 M  $\text{KNO}_3$  as the supporting electrolyte which was acidified to 0.5% with  $\text{HNO}_3$ . The whole electroplating process was controlled by the home made instrument. The FTSV deposition response was recorded during a 300 s potential excitation. The parameters were set as follows: bias potential:  $-0.2 \text{ V}$  (vs. SCE.), amplitude: 100 mV, frequency: 160 Hz, quiet time: 2 s. The amplitude setting was chosen with the consideration of the following two factors. Firstly, the ac response as well as the potential window of the obtained voltammogram will be small and narrow if the amplitude of the ac signal is too small; secondly, it becomes hard to observe the mercury film coalescence events if the amplitude of the ac signal is too large.

In order to reveal the mechanism of mercury film surface oxidation, the same electroplating procedure was applied as described above. After the mercury film was plated, the microelectrode was taken out and rinsed by ultrapure water for 1 min and then inserted in another cell, which contained only 0.1 M  $\text{KNO}_3$  electrolyte solution. The parameters for mercury oxidation investigation were set as follows: amplitude: 200 mV, frequency: 160 Hz, quiet time: 0.1 s. The reason of setting parameter of quiet time as 0.1 s was that the reduction of oxides was quite fast as the mercury film tended to reunite instantly as soon as the electrode was connected on. Relevant details will be discussed in the coming sections.

## 3. Results and discussion

### 3.1. Mercury electroplating by chronoamperometry method

Before carrying out experiments with UME, we electroplated mercury on a GCE by chronoamperometry, and with the simple intention of reproducing the phenomena reported by previous publications. In Fig. 1A, many spikes can be observed after 50 s, and the density of current spike increases along with time. The spikes are believed to be originated from the interaction between the mercury droplets. As can be seen in Fig. 1B, numerous droplets are formed on the surface of GCE and contact as well as further interaction is unavoidable. However, except for the trend of increasing density, the sharp spike (the insert in Fig. 1A) has no ability to reflect anything else about the surface morphology or properties of individual mercury droplets, since the noise or other irrelevant signals are easily mistaken for the signals of mercury droplets coalescence. In contrast to this experiment, UME was applied to enhance the sensitivity, and FTSV could provide not only time domain response but also frequency domain response, which provided much more information about interfacial interaction of individual droplets.

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