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Underpotential deposition of lead on quasi-spherical and faceted gold nanoparticles

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ABSTRACT

The underpotential deposition of lead was studied on spherical and faceted gold nanoparticles. On 21.7 nm spherical nanoparticles, a single stripping peak from Au(111) face was observed at -0.2 V, whereas on 82 nm faceted gold nanoparticles the peak split in to two at -0.2 V and -0.18 V vs Ag/AgCl (3 M KCl). The roughening of the Au(111) terraces by electrochemical treatment leads to the suppression of the spike. It appears that the extent of surface crystallinity of nanoparticles causes the observed differences in the upd-stripping behaviour. The splitting of the Pb-upd stripping peak from Au(111) face can be used as an indication for the surface crystallinity of gold nanoparticles.

1. Introduction

Underpotential deposition has been used to probe the surface structure as it is sensitive to the steps and terraces of stepped single crystal surfaces [1–4]. Underpotential deposition of lead (Pb-upd) or copper (Cu-upd) on Au, Ag, Pt etc. [5] has been studied in detail as it provides unique finger-prints of the surfaces. Pb-upd has been successfully applied to decipher the surface structure of gold nanostructures [6]. The structural information thus obtained from Pb-upd has been used to understand electrode processes such as oxygen reduction [6], methanol oxidation [7,8], glucose oxidation [9], etc., which are surface sensitive reactions [10–12]. Still, the wealth of information available in the single crystal gold research has not been fully applied to complex systems like bulk gold and gold nanoparticle surfaces [13] and thus more efforts are necessary. We performed Pb-upd on spherical gold nanoparticles and faceted gold nanoparticles. The results revealed that on spherical particles, a Pb-upd stripping peak was observed at -0.2 V related to the Au(111) face, whereas a “doublet peak” [2,6] (a peak at -0.2 V vs. Ag/AgCl (3 M KCl) and a spike at -0.18 V vs. Ag/AgCl (3 M KCl)) like on an Au(111) single-crystal electrode was observed on faceted Au nanoparticles. Schultze et al. [1] reported that the doublet peak results from slow kinetics of lead stripping. Based on STM studies, Tao et al. [14] showed that island formation and coalescence lead to the splitting of the adsorption peaks into two, but an explanation for the splitting of stripping peak was not provided. In the light of our result it appears that with smaller terraces with more steps and defects, a doublet peak was not observed even at 0.1 V s⁻¹ scan rate, but it was

observed on a faceted particle at 0.02 V s⁻¹. Also, the electrochemical cleaning by deposition/dissolution of PbO₂ film [8] resulted in the suppression of the spike at 0.02 V s⁻¹. Possibly, the well oriented nanocrystals have well-grown terraces of Au(111) that resulted in a doublet peak similar to the extended Au(111) terraces and the cleaning potential cycles could eventually introduce such a degree of roughness on the terraces, that the spike at -0.18 V vs. Ag/AgCl (3 M KCl) is suppressed.

2. Experimental

Perchloric acid (Merck, 70%, 99.999% purity relating to trace metals), Sodium perchlorate (Alfa-Aesar, 98.0–102.0%), lead perchlorate (Sigma-Aldrich, $\geq 99.995\%$), potassium nitrate (Merck, Emsure® for analysis), but-2-yne-1,4-diol (Sigma-Aldrich) were used as obtained. All the solutions were prepared using Millipore water (18.2 M Ω cm) and the temperature was maintained at 25 °C.

Gold nanoparticles (AuNPs) were synthesized using but-2-yne-1,4-diol (BD) solutions as a reducing agent as reported earlier [15]. To get spherical nanoparticles, the solution composition was: 0.25 mM HAuCl₄ + 2.5 mM BD (1:10 ratio). For faceted nanoparticles, we used 0.25 mM HAuCl₄ + 0.175 mM BD (1:0.7 ratio). HAuCl₄ solutions, standardised by ICP-MS, were prepared by dissolution of gold in aqua regia [16]. The AuNPs were characterized by transmission electron microscopy (TEM) using 120 kV, JEM 1210 microscope.

A three-electrode cell configuration connected to Autolab potentiostat (from Metrohm) was used for electrochemical experiments in

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quiescent solution. A glassy carbon (GC) electrode ($\varnothing = 3$ mm) was used as working electrode. The electrode was mechanically polished using 1 μm , 0.3 μm and 0.05 μm Al_2O_3 slurries on a polishing pad (from Buhler) successively, cleaned well by sonication in Millipore water for 2 min and finally rinsed with Millipore water. The AuNPs were deposited on the GC electrode by drop casting and drying. The spherical and faceted gold nanoparticles deposited on GC electrode are denoted as sp-AuNPs/GC and ft-AuNPs/GC, respectively. A GC rod (from Metrohm) was used as a counter electrode, and an Ag/AgCl (3 M KCl) electrode (from Metrohm) as a reference ($E^0 = 0.210$ V vs SHE). The reference electrode was separated from the electrolyte by KNO_3 -agar salt bridges (polyethylene tubing filled with the salt-gel). The Pb-upd experiment was performed in deaerated solution of 0.1 M $\text{NaClO}_4 + 0.01$ M HClO_4 mixture containing 1 mM $\text{Pb}(\text{ClO}_4)_2$ solutions. The potential was fixed at -0.42 V for 60 s to obtain the underpotential deposit and the deposit was stripped by employing anodic potential sweeps at a scan rate of 0.02 V s^{-1} . In cyclic experiments, a scan rate of 0.02 V s^{-1} was used for cathodic deposition and anodic dissolution of upd-Pb. Unless otherwise mentioned, the electrolytes were deaerated by bubbling N_2 for 20 min before the measurements and a N_2 blanket was maintained throughout the experiment.

3. Results and discussions

The Fig. 1A & B show the representative TEM images of the AuNPs synthesized by reducing HAuCl_4 with but-2-yne-1,4-diol [15]. The 1:10 ratio of reactants produced almost quasi-spherical (less faceted) nanoparticles (Fig. 1A), while 1:07 ratio produced well-faceted nanoparticles (Fig. 1B). The mean particle size/mean edge length of quasi-spherical nanoparticles was 21.7 ± 3.5 nm/ 10.3 ± 0.7 nm and of larger faceted nanoparticles was 82 ± 27 nm/ 10.3 ± 0.7 nm. The morphology of the faceted nanoparticles was not very regular.

The surface characteristics of these particles deposited on a GC electrode were assessed by Pb-upd. Fig. 2A & B show the upd-Pb deposition and a dissolution curves recorded on sp-AuNPs/GC and ft-AuNPs/GC (as-deposited and cleaned) at a scan rate of 0.02 V s^{-1} . The cleaning was performed as proposed by Hernandez et al. [8] with PbO_2 film deposition and dissolution during potential cycling between 0.5 V to 1.6 V vs Ag/AgCl (3 M KCl) at a scan rate of 0.1 V s^{-1} for 10 cycles in acidic solutions. The cycles for the PbO_2 formation and dissolution comprised also the potentials for gold oxidation and gold oxide reduction (CV is not shown).

On as-deposited sp-AuNPs/GC, the Pb-upd curve showed two stripping peaks, 1a and 1a' at -0.35 V and 0.017 V corresponding to terraces (< 4 -atom width) and steps of Au(110), respectively [2], and a

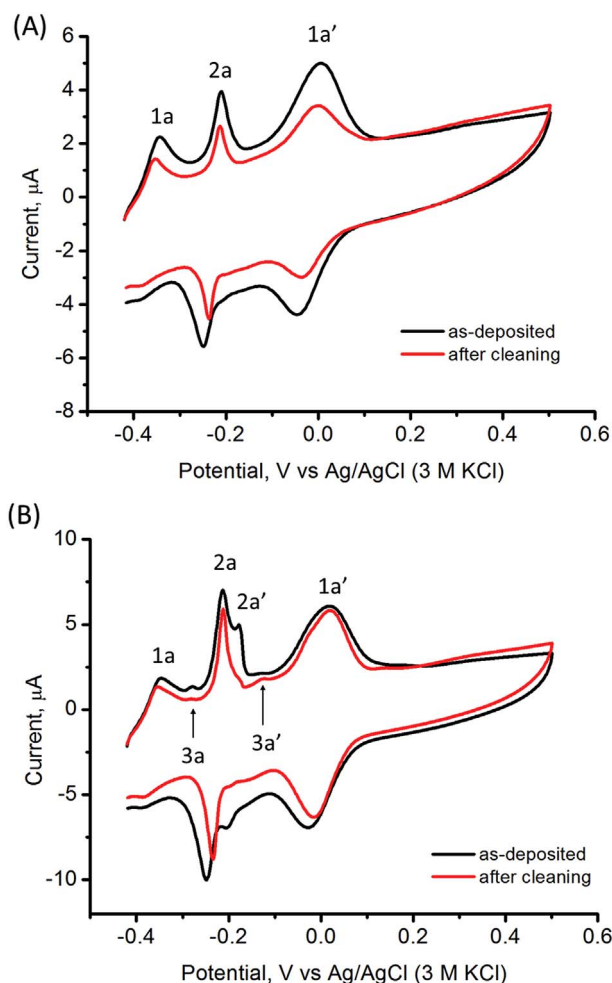


Fig. 2. Pb-upd curves recorded on as-deposited (black curve) and cleaned (red curve) gold nanoparticles at a scan rate of 0.02 V s^{-1} : (A) sp-AuNPs/GC and (B) ft-AuNPs/GC. The arrow indicates the disappearance of the spike at -0.18 V. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

peak 2a at -0.2 V that is related to the Au(111) face. However, on as-deposited ft-AuNPs/GC, we noticed a spike 2a' at -0.18 V and two other tiny peaks at -0.28 V and -0.12 V in addition to those observed on spherical particles. The latter two peaks (3a and 3a') were ascribed

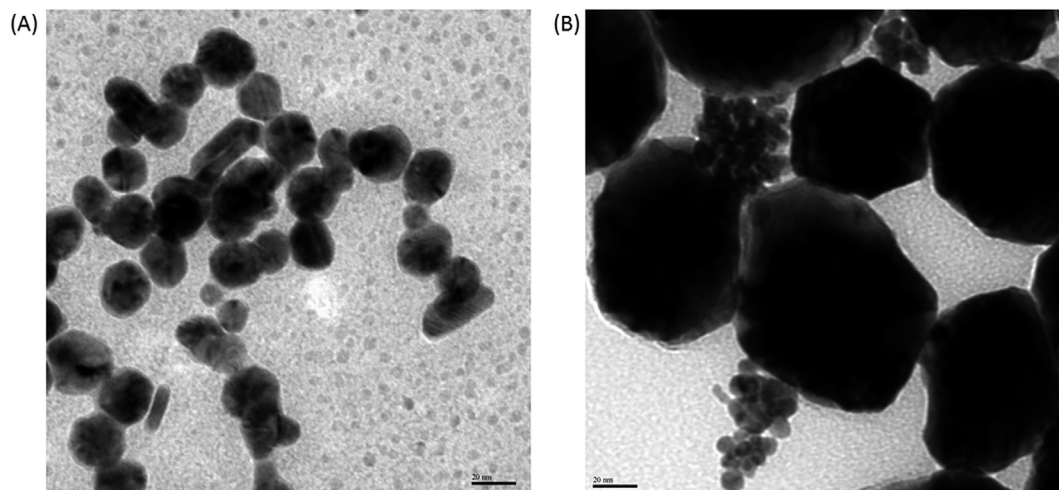


Fig. 1. TEM micrograph of AuNPs: (A) spherical and (B) faceted nanoparticles. Scale bar = 20 nm.

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