



# Studies on deposition of gold atomic clusters on to polycrystalline gold electrode from aqueous cetyl trimethyl ammonium bromide solutions



Sindhu R. Nambiar, Padamadathil K. Aneesh, Talasila P. Rao\*

Chemical Sciences & Technology Division (CSTD), CSIR–National Institute for Interdisciplinary Science & Technology (CSIR–NIIST), Trivandrum 695019, India

## ARTICLE INFO

### Article history:

Received 16 January 2014

Received in revised form 3 March 2014

Accepted 6 March 2014

Available online 15 March 2014

### Keywords:

Gold atomic clusters

Cationic surfactant aided dissolution and deposition

Surface and bulk layer dissolution deposition

Electro-catalytic activity

## ABSTRACT

Atomic (molecular) clusters, with less than 50–100 atoms (size  $\leq 1.5$  nm) are of special interest and exhibit novel and interesting properties due to quantum confinement of electrons and holes. These properties are quite different from those of gold nanoparticles and hence, understanding of electrochemical phase formation of gold atomic clusters assumes importance. In the present study, we report a detailed investigation of deposition of gold atomic clusters on to polycrystalline gold electrode from aqueous cationic surfactant solutions. The studies were undertaken over a wide range of potentials, covering both surface and bulk layer dissolution and deposition processes, by means of cyclic voltammetric and chronoamperometric techniques. Thus, gold atomic clusters are formed in both surface and bulk layer dissolution and deposition processes as evidenced by AFM, MALDI-TOF, XPS and DLS. Electrocatalytic activity has been performed by the electrochemical reduction of oxygen ( $O_2$ ) on AuAC modified gold electrode in 0.1 M  $H_2SO_4$ .

© 2014 Elsevier B.V. All rights reserved.

## 1. Introduction

Atomic clusters are unique materials formed at the crossroad of atomic species and nanoparticles, exhibiting exciting optoelectronic and catalytic properties. Gold atomic clusters are of particular interest due to its fascinating properties and potential applications in catalysis [1,2], biology [3], non-linear optics [4,5], electronics [6,7], sensors [8–10] and other domains of high technology and medicine [11]. Metal deposition for a long time has attracted special attention in research and development mostly due to its great technological importance. Gold is frequently regarded as the ideal metal for the investigation of solid electrode behavior, which in aqueous media is often considered as a metal which is highly resistant to dissolution [12] and it possesses very weak chemisorbing properties and an extensive double layer region that exhibit monolayer dissolution/formation at quite negative potentials. Metal electrodeposition for a long time has attracted special attention in research and developments mostly due to its great technological importance. Recently, significance in the underpotential electrodeposition of elements has increased essentially due to potential applications in several fields of technology such as photovoltaics and electrocatalysis. Electrochemical phase formation (ECPF) studies are fascinating in terms of its simplicity

and deeper insight and exhibits a different domain of knowledge which will open a new arena of synthetic uniqueness backed with theoretical understanding. Electrochemistry is an ideal tool for analyzing the complex process of dissolution–adsorptive formation of adatoms through phase formation studies. The two primary classes of models for electrochemical phase formation (ECPF) on smooth surfaces are based on nucleation–growth and adsorption respectively. Formation of metal adatoms (Me) on polycrystalline inert metals as foreign substrates was initially studied using radiotracer measurements by Haissinski et al. [13], Rogers et al. [14] and Frumkin et al. [15]. In 1980's, important information on the structure of metal adatoms ( $Me_{ads}$ ) over layers, the mechanism of two dimensional (2D)  $Me_{ads}$  overlayer formation, and UPD–OPD transition processes was obtained by in situ application of surface analytical methods like X-ray scattering, second harmonic generation and local probe techniques which give lateral atomic resolution [16].

Synthesis of metal clusters can be divided into three distinct stages: (1) nucleation, (2) evolution of nuclei into seeds, and (3) growth of seeds into nanocrystals. In practice, structures characteristic of kinetically controlled syntheses can be achieved by: (1) substantially slowing down precursor decomposition or reduction, (2) using a weak reducing agent, (3) coupling the reduction to an oxidation process, or (4) taking advantage of Ostwald ripening. The production of very small clusters opens a fascinating method of producing multiple nanostructures with different properties by combining/assembling sub-nm elemental pieces. They exhibit discrete energy levels with molecule-like transitions and thus

\* Corresponding author. Tel.: +91 471 2515317; fax: +91 471 2491712.

E-mail address: [tprasadarao07@gmail.com](mailto:tprasadarao07@gmail.com) (T.P. Rao).

provide a “missing link” between atomic and nanoparticle behavior. Reactivity and catalytic properties of these clusters depend on the cluster size and the support and are distinct from those of supported particles that resemble bulk metals. Advantages of electrochemical methods over chemical ones in synthesis of metal nanostructures are the high purity products and good control of size, shape and morphology of the nanostructured materials. Reetz et al. [17] have demonstrated the size-selective synthesis of tetraalkylammonium-stabilized Pd and Ni clusters by a simple electrochemical process. Tetraalkyl ammonium salts are used as both supporting electrolyte and stabilizer for the cluster formation. Temperature dependent size-controlled gold nano clusters were synthesized electrochemically by El-Sayed group from micellar solutions [18]. Rapid synthesis of a large quantity of uniform-sized gold nano cubes was achieved galvanostatically, using a surfactant cetyl trimethyl ammonium bromide (CTAB) solution and acetone [19]. Lopez-Quientela group have prepared gold [20], copper [21] and silver [22] atomic clusters by an analogous method employing tetrabutyl ammonium bromide as supporting electrolyte and stabilized in acetonitrile medium. Phani's group [23] have synthesized gold atomic clusters from aqueous CTAB solutions employing potentiodynamic method. We have developed hybrid gold atomic cluster- cobalt oxide composite electrode for cysteine sensing [8]. Recently, Workentin et al. [24] have reported the electrochemistry of robust gold nanoparticle suggesting that a specie is desorbed from the surface during the oxidative scan and partially re-adsorbed during the reductive scan. We have reported the synthesis and electrochemical phase formation of mixed monolayer protected gold atom-oxide clusters based on theoretical models for metal deposition [9]. Fundamental understanding of the formation of atomic clusters assumes importance as it can reveal a whole lot of information on the atomic level-nanoparticle transition states.

Properties of atomic clusters are quite different from those of gold nanoparticles and hence, understanding ECPF of gold atomic clusters assumes importance in biomedical diagnostics. In the present study we report for the first time a detailed investigation on the ECPF of cationic surfactant stabilized ion pair and atomic clusters of gold in surface and bulk layer dissolution and deposition regions based on reported theoretical models. Cetyl trimethyl ammonium bromide was used as both supporting electrolyte and stabilizer for the cluster formation. In addition to electrochemical elucidation of ECPF of gold clusters, extensive spectral and morphological characterizations are also described. For application purpose, the electrocatalytic activity of AuAC toward oxygen reduction reaction was also assessed in the acidic medium by cyclic voltammetry.

## 2. Experimental methods

### 2.1. Materials

Cetyltrimethyl ammonium bromide (CTAB), cetyl pyridinium bromide (CPB), sodium dodecyl sulphate (SDS) and Tween 80 were purchased from Aldrich, Milwaukee, WI, USA. Working solutions were prepared using de-ionized double distilled water. All other chemicals were of analytical reagent grade (E Merck, Mumbai, India) and were used as received without further purification. All experiments were carried out at ambient temperature.

### 2.2. Characterization

Electrochemical experiments were performed on a  $\mu$ -Autolab electrochemical work station (Ecochemie, Netherlands) with a conventional three electrode cell. The system was run on a PC using GPES 4.9 software. Working electrode was Au disc with geometric

surface area of 0.0314 cm<sup>2</sup>. Reference electrode and counter electrode used were Ag/AgCl (in saturated KCl solution) and platinum sheet respectively. The gold atomic clusters deposited on gold disc electrode were sonicated into CTAB or water solutions and subjected to spectral and morphological characterization. MALDI-TOF MS spectra were measured on a Voyager DE Pro (Applied Biosystems) using  $\alpha$ -cyano-4-hydroxy cinnamic acid as the matrix. X-ray photoelectron spectroscopic analyses were carried out on a KRATOS AXIS 165 X-ray Photoelectron Spectrometer (IICT-Hyderabad, India). Dynamic Light Scattering experiment was conducted using a Malvern Instruments zetasizer nano Zis Model No: ZEN 3600 to determine the particle size. The size and morphology was characterized by high-resolution transmission electron microscopy (HRTEM) on a FEI, TECNAI 30G2 S-TWIN microscope with an accelerating voltage of 300 kV.

### 2.3. Gold cluster synthesis and electrode modification

Prior to modification, bare gold electrode was polished to a mirror finish using 0.5  $\mu$ m alumina slurries. After each polishing, the electrode was sonicated in de-ionized double distilled water for 5 min in order to remove adsorbed substances from the electrode surface. Gold atomic clusters were synthesized electrochemically by potentiodynamic method by cycling the gold electrode in 50 mM CTAB solutions in the potential range 0–1.2 V with a sweep rate of 50 mV/s (Fig. S1) During the electrochemical cycling it is expected that the Au<sup>+</sup> formed during the anodic scan will get reduced to Au<sup>0</sup> during the cathodic scan and, due to the high aurophilic interaction, Au adatoms get stabilized to form Au clusters. Gold atomic clusters, due to their high surface to volume ratio, attain excess electron density at surfaces which is being stabilized by the positively charged cetyl ammonium moieties.

## 3. Results and discussion

### 3.1. Cyclic voltammetric studies

Gold atomic clusters were synthesized by subjecting the polycrystalline gold electrode to potentiodynamic cycling in the potential range 0–1.2 V in presence of cationic (CTAB or CPB), anionic (sodium dodecyl sulphate) and neutral (Tween 80) surfactants at concentrations of 50 mM at a scan rate of 50 mV/s (Fig. S2A). During anodic scan gold electrode undergo dissolution to form Au<sup>+</sup> ions [25] which will get stabilized by bromide ions of micellar solution of CTAB and while reversing the scan Au<sup>+</sup> ions undergo reduction to form Au(0) clusters. Since the experiment is carried out in quiescent solution and using a stationary electrode the Au clusters do not desorb from the electrode surface. When KBr was used instead of CTAB it was observed that gold get dissolved during the anodic scan and get diffused from the electrode surface to the solution. Hence, it can be concluded that micellar solution of CTAB plays a major role in stabilization and deposition of the gold atomic clusters on the gold electrode surface. Different surfactants were tried and it was observed that gold atomic clusters were formed only in presence of cationic surfactant solutions (CTAB/CPB) and not with anionic and neutral surfactants like SDS and Tween 80 or KBr.

Fig. S2B shows potentiodynamic I-E profiles obtained at different concentrations of CTAB. Redox peaks were observed when concentration of CTAB is above >0.1 mM (the critical micelle concentration of CTAB) which indicates that gold clusters were formed only at higher concentration of CTAB. Fig. 1 shows the potentiodynamic I-E curves drawn in presence of CTAB by restricting anodic potential scan limits to 0.8 and 1.2 V. Three distinct regions were obtained in I-E profiles with distinct anodic and cathodic peaks

Download English Version:

<https://daneshyari.com/en/article/218773>

Download Persian Version:

<https://daneshyari.com/article/218773>

[Daneshyari.com](https://daneshyari.com)