Au Electrodeposition at the Liquid-Liquid Interface: mechanistic aspects☆

Akihiro Uehara [a,b,*], Teruo Hashimoto [c], Robert A.W. Dryfe [a,*]

[a] School of Chemistry, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom
[b] Division of Nuclear Engineering Science, Research Reactor Institute, Kyoto University, Asashironishi, Kumatori, Osaka, 590-0494, Japan
[c] School of Materials, University of Manchester, Oxford Road, Manchester, M13 9PL, United Kingdom

ABSTRACT

The deposition mechanism of metallic gold was investigated based on charge transfer voltammetry at the water/1,2-dichloroethane (W/DCE) interface, and the corresponding redox voltammetry of the metal precursor in W and the reductant, triphenylamine (TPA), in DCE. The metal precursor was present as Au(III) ($AuCl_4^-$), or Au(I) ($AuCl_2^-$) in W or DCE. Electron transfer could be observed voltammetrically at the interface between W containing both Au precursors and DCE containing TPA. Au particles, formed by constant potential electrolysis at the W/DCE interface, were examined by transmission electron microscopy. It was shown that deposit size could be controlled via the applied potential and time, with specific conditions to form particles of less than 10 nm identified.

© 2014 The Authors. Published by Elsevier Ltd. All rights reserved.

1. Introduction

The combination of nanotechnology with chemistry, biology, physics, and medicine for the development of ultrasensitive detection and imaging methods in the analytical or biological sciences is becoming increasingly important. Nanoparticle synthesis, at or near the interface between two immiscible liquids has been known since the time of Faraday [1] but it is only in the last two decades or so, with the advent of appropriate microscopic characterization, that the systematic investigation of the relationship between particle size and growth conditions has become more established. A huge variety of nanoparticles has been synthesized, with immiscible liquids frequently used in synthesis [2]. The deposition process at an interface between two immiscible liquids can be considered as an intermediate case between purely homogeneous deposition through electron transfer between redox couples in the same phase, which as a spontaneous process is difficult to control, and heterogeneous deposition at the (conventional) solid electrode-electrolyte interface [3]. Separation of the two reactants, the oxidised metal precursor and a reducing agent, by the

liquid-liquid interface means the driving force of nucleation can be controlled through the interfacial potential.

In fact, the electrochemical synthesis of nanoparticles at liquid-liquid interfaces is a relatively new field of research. Charge (electron and ion) transfer reactions at the two immiscible electrolyte solutions have been studied extensively using simple reversible systems, whereas electrochemical synthesis has only been described in a limited number of cases.

The potential controlled electrodeposition of various metals, e.g. Au [4–10], Cu [11], Pd [12–16], Pt [15–17], and Ag [18–22] has been investigated at organic-water interfaces. Other studies of the spontaneous growth process have been carried out using the interfacial potential established through spontaneous transfer of a partitioning ion between the water and organic phases (Nernst partition equilibrium) [12,16,22,23]. Characterization of the initial nucleation process was a focus of some of this work [12]. In order to apply to the formation of nanoparticles, it is important to rationalise the deposition process in terms of existing models of phase formation. To this end, some results for the deposition of metallic Pd at the liquid-liquid interface by a reductant in organic solution have been reported [12,13,15,16,24,25], whereas deposition of metallic gold at the liquid-liquid interface was limited because of the large differences in redox potential between Au ion and reductants [4,6,7]. Furthermore, precise experimental control over nanoparticle size via the potential applied to the liquid-liquid interface has not been described to date, although deposition at the interface has been probed by UV-Vis and X-ray absorption spectroscopy [26]. To prevent nanoparticle aggregation, tetraalkylammonim halides such as

cetyltrimetylammonium bromide, CTAB, and tetraoctylammonium chloride, TOACl, have been widely used as the capping ligands forming monolayers on particle surfaces [27–29]. Cunnane and co-workers [5,9,10] have previously investigated the effect of deposition conditions for the case of Au deposition at the liquid-liquid interface. In their work, Au was not reduced heterogeneously via an organic phase electron donor, rather the $AuCl_4^-$ was transferred from the organic phase to the aqueous phase. Following transfer, the $AuCl_4^-$ underwent a spontaneous homogeneous reduction with an aqueous phase electron donor to form a gold-polymer composite. Both tyramine and resorcinol were used as the electron donors, and the influence of solution pH and applied interfacial potential were investigated. An approximately linear relation between particle diamater (in the range 17 to 35 nm) was found with applied potential, although it is not clear if the Nernst equilibrium included the effect of the $AuCl_4^-$ ion distribution in this case.

In the present study, Au deposition at the water/1,2-dichloroethane (W/DCE) interface was performed with $AuCl_4^-$ and dichloroaurate ($AuCl_2^-$) dissolved in either W or DCE. The Au precursors react at the interface with a hydrophobic amine reductant, triphenylamine, dissolved in DCE, which results in the reduction of $AuCl_4^-$ and $AuCl_2^-$ to form metallic Au. Au deposition at this interface is a relatively complex process. In spite of the interest in Au nanoparticle synthesis at liquid-liquid interfaces, there are few electrochemical studies of Au interfacial deposition. Here, charge (electron and ion) transfer was observed by voltammetry at the W/DCE interface to probe the deposition mechanism. Furthermore, the Au deposit was analyzed by transmission electron microscopy and the effect of the applied potential at the interface and the duration of the electrolysis was investigated.

2. Experimental

2.1. Chemicals

Hydrogen tetrachloroaurate, $HAuCl_4 \cdot 3H_2O$ (Alfa, $\geq$ 99.999%) was used as the source of Au(III), tetrabutylammonium dichloroaurate, $TBA^+AuCl_2^-$ (Tokyo Kasei, $\geq$ 99.99%) was used as the Au(I) source. HCl was used as a supporting electrolyte. 1,2-dichloroethane, DCE ($\geq$ 99%, Aldrich) was used as the organic solvent. Triphenylamine (TPA, $\geq$ 99%, Acros Organics) was used as reductant in DCE. The tetraoctylammonium (TOA^+) salt of $AuCl_4^-$ in DCE was prepared by shaking an equimolar volume of $HAuCl_4$ in W and TOA^+Cl^- in DCE for the $TOA^+AuCl_4^-$ case. The TOA^+ salt of $AuCl_2^-$ in DCE was prepared by shaking pure W with equimolar amounts of $TBA^+AuCl_2^-$ and TOA^+Cl^- in DCE. The supporting electrolyte in DCE for potential sweep experiments was TOA^+TFPB^- or $BTPPA^+TFPB^-$, where $BTPPA^+$ and $TFPB^-$ denote bis(triphenylphosphoranylidene) ammonium cation and tetrakis[3,5-bis(trifluoromethyl)phenyl] borate anion, respectively. $BTPPA^+TFPB^-$ was obtained as a precipitate after mixing a methanol solution of $BTPPA^+Cl^-$ with a methanol solution of Na^+TFPB^-, and was purified by recrystallization from ethanol based on the temperature dependence of the solubility of the salt.

2.2. Measurement of the voltammogram for charge transfer at the macro and micro W/DCE interfaces

Two electrochemical cells were employed; a macro-interface cell and a micro-interface cell. In the (conventional) macro-interface case, cyclic voltammetry experiments were performed using a four electrode configuration with an IVIUM potentiostat ("Compactstat" model, IVIUM Technologies, the Netherlands). No iR compensation was applied for the electrochemical measurements: it was assumed that a sufficient concentration of supporting electrolytes was present in both phases. Homemade Ag/AgCl and platinum gauze were used, respectively, as reference electrodes (RE) and counter electrodes (CE). The organic CE was insulated from the W phase by coating its contact in a glass sheath.

The cell used for the electrochemical measurements at the W/DCE interface had a cross-sectional area of about 0.64 cm^2 and had a volume of 3 cm^3. Further details are described elsewhere [7]. The micro-interface cell uses a 16 μm thick polyester film, with a micro hole 30 μm in diameter, to separate the W and DCE phases [30–32].

The potential difference at the W/DCE interface, E, was measured vs the potential of a silver-silver chloride electrode, SSE, in W referred to the potential of a $BTPPA^+$ ion selective electrode [33], inserted in DCE. The generic cell composition is:

Ag | AgCl | 10 mM LiCl (W) | W1 (W) || DCE1 (DCE) | 10 mM $BTPPA^+TFPB^-$ (DCE) | 1 mM $BTPPA^+Cl^-$ + 10 mM LiCl (W) | AgCl | Ag

The E is related to the Galvani potential difference, $\Delta_{DCE}^W \phi$, as.

$$E = \Delta_{DCE}^W \phi + E_{ref} \tag{1}$$

where E_{ref} is the potential of the reference electrodes employed. In the calculation of $\Delta_{DCE}^W G^o (= -zF\Delta_{DCE}^W \phi^o)$, the measured E was converted using the extrathermodynamic assumption of Parker [34]. Cell compositions used in this work were summarised in Table 1.

2.3. Electrochemical deposition

Electrochemical deposition was performed using a constant potential for a defined time: the DCE was then separated from W and stored in a glass vial. Immediately prior to transmission electron microscopy, TEM (JEM-2000FX II, JEOL), DCE was dropped on to the TEM grid (Holey carbon films on 300 mesh grids, Agar Scientific) to isolate the deposit.

3. Results and discussion

3.1. Electrochemical reaction between Au species and TPA

3.1.1. Voltammetry of Au deposition using $AuCl_4^-$ dissolved in W

Initially, voltammograms were recorded using W containing $AuCl_4^-$ and supporting electrolyte, and DCE solution without reductant (TPA) to confirm the effect of the latter on the interfacial charge transfer process. Curve 1 in Fig. 1 shows the voltammogram for the transfer of $AuCl_4^-$ between W and DCE. The transfer reaction for the positive and negative current, I_{p1} and I_{n1}, is quasi-reversible and the mid-point potential is calculated to be 0.115 V (Eq. (2)).

$$AuCl_4^-{}_{(DCE)} \rightleftharpoons AuCl_4^-{}_{(W)} \tag{2}$$

Table 1
Cell compositions used in this work.

W1	DCE1	
0.2 mM HAuCl$_4$	10 mM TOA$^+$TFPB$^-$	Cell 1
10 mM HCl		Fig. 1
0.5 mM HAuCl$_4$	20 mM TPA	Cell 2
10 mM HCl	10 mM TOA$^+$TFPB$^-$	Fig. 2, 4
0, 0.1, 0.2, 0.4 mM	20 mM TPA	Cell 3
HAuCl$_4$	1 mM TOA$^+$TFPB$^-$	Fig. 5
10 mM HCl		
10 mM HCl	0.5 mM TOA$^+$AuCl$_4^-$	Cell 4
	10 mM TOA$^+$TFPB$^-$	Fig. 6(a)
10 mM HCl	0.5 mM TOA$^+$AuCl$_4^-$	Cell 5
	20 mM TPA	Fig. 6(b)
	10 mM TOA$^+$TFPB$^-$	
10 mM HCl	0.5 mM TOA$^+$AuCl$_2^-$	Cell 6
	10 mM TOA$^+$TFPB$^-$	Fig. 7(a)
10 mM HCl	0.5 mM TOA$^+$AuCl$_2^-$	Cell 7
	20 mM TPA	Fig. 7(b)
	10 mM TOA$^+$TFPB$^-$	