Au Electrodeposition at the Liquid-Liquid Interface: mechanistic aspects

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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 precursors in W and the reductant, triphenylamine (TPA), in DCE. The metal precursor was present as Au(III) \(\text{[AuCl}_2\text{]}^\text{−}\), or Au(I) \(\text{[AuCl}_4\text{]}^\text{−}\) 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.

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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 \cite{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 \cite{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 \cite{3}. Separation of the two reagents, 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 \cite{4–10}, Cu \cite{11}, Pd \cite{12–16}, Pt \cite{15–17}, and Ag \cite{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) \cite{12,16,22,23}. Characterization of the initial nucleation process was a focus of some of this work \cite{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 \cite{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 \cite{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 \cite{26}. To prevent nanoparticle aggregation, tetraalkylammonium halides such as cetyltrimethylammonium 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 AuCl₄⁻ was transferred from the organic phase to the aqueous phase. Following transfer, the AuCl₄⁻ 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 diameter (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 AuCl₄⁻ ion distribution in this case.

In the present study, Au deposition at the water/1,2-dichloroethane (W/DCE) interface was performed with AuCl₄⁻ and dichloroaurate (AuCl₂⁻) dissolved in either W or DCE. The Au precursor reacts at the interface with a hydrophobic amine reductant, triphenylamine, dissolved in DCE, which results in the reduction of AuCl₄⁻ and AuCl₂⁻ 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, HAuCl₄ 3H₂O (Alfa, ≥ 99.999%) was used as the source of Au(III), tetrabutylammonium dichloroaurate, TBA⁺AuCl₂⁻ (Tokyo Kasei, ≥ 99.99%) was used as the Au(I) source. HCl was used as a supporting electrolyte. 1,2-dichloroethane, DCE (≥ 99%, Aldrich) was used as the organic solvent. Triphenylamine (TPA, ≥ 99%, Acros Organics) was used as reductant in DCE. The tetracylammonium (TOA⁺) salt of AuCl₄⁻ in DCE was prepared by shaking an equimolar volume of HAuCl₄ in W and TOA⁺Cl⁻ in DCE for the TOA⁺AuCl₄⁻ case. The TOA⁺salt of AuCl₄⁻ in DCE was prepared by shaking pure W with equimolar amounts of TBA⁺AuCl₂⁻ and TOA⁺Cl⁻ in DCE. The supporting electrolyte in DCE for potential sweep experiments was TOA⁺TFPB⁻ or BTPA⁺TFPB⁻, where BTPA⁺ and TFPB⁻ denote bis(triphenylphosphoranylidene)ammonium cation and tetrais[3,5-bis(trifluoromethyl)phenyl]borate anion, respectively. BTPA⁺TFPB⁻ was obtained as a precipitate after mixing a methanol solution of BTPA⁺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 cm² and had a volume of 3 cm³. 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 BTPA⁺ ion selective electrode [33], inserted in DCE. The generic cell composition is:

\[
\text{Ag} | \text{AgCl} | 10 \text{mM LiCl (W)} | W | \text{DCE (DCE)} | 10 \text{mM BTPA⁺TFPB⁻ (DCE)} | 10 \text{mM LiCl (W)} | \text{AgCl | Ag}
\]

The \( E \) is related to the Galvani potential difference, \( \Delta W_{\text{DCE}} \phi \), as:

\[
E = \Delta W_{\text{DCE}} \phi + E_{\text{ref}}
\]

where \( E_{\text{ref}} \) is the potential of the reference electrodes employed. In the calculation of \( \Delta W_{\text{DCE}} \phi = -2F \Delta W_{\text{DCE}} \phi \), 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 AuCl₄⁻ dissolved in W

Initially, voltammograms were recorded using W containing AuCl₄⁻ 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 AuCl₄⁻ between W and DCE. The transfer reaction for the positive and negative current, \( i_p \) and \( i_n \), is quasi-reversible and the mid-point potential is calculated to be 0.115 V (Eq. (2)).

\[
\text{AuCl}_4^- \text{(DCE)} \rightleftharpoons \text{AuCl}_4^- \text{(W)}
\]

Table 1

| Cell compositions used in this work. |
|-------------------|
| W1                   | DCE1                  |
| 0.2 mM HAuCl₄       | 10 mM TOA⁺TFPB⁻       | Cell 1 |
| 10 mM HCl           | 20 mM TPA             | Fig. 1 |
| 0.5 mM HAuCl₄       | 10 mM TOA⁺TFPB⁻       | Cell 2 |
| 10 mM HCl           | 20 mM TPA             | Fig. 2, 4 |
| 0, 0.1, 0.2, 0.4 mM | 10 mM TOA⁺TFPB⁻       | Cell 3 |
| AuCl₄⁻              | 10 mM TOA⁺TFPB⁻       | Fig. 5 |
| 10 mM HCl           | 0.5 mM TOA⁺AuCl₄⁻      | Cell 4 |
| 10 mM HCl           | 10 mM TOA⁺TFPB⁻       | Fig. 6(a) |
| 0.5 mM TOA⁺AuCl₄⁻   | 20 mM TPA             | Cell 5 |
| 10 mM HCl           | 10 mM TOA⁺TFPB⁻       | Fig. 6(b) |
| 10 mM HCl           | 0.5 mM TOA⁺AuCl₄⁻      | Cell 6 |
| 10 mM HCl           | 10 mM TOA⁺TFPB⁻       | Fig. 7(a) |
| 10 mM HCl           | 0.5 mM TOA⁺AuCl₄⁻      | Cell 7 |
| 10 mM HCl           | 20 mM TPA             | Fig. 7(b) |
The current at the negative vertex (−0.30 V) corresponds to the transfer of Cl⁻ from the supporting electrolyte between W and DCE. Scans to more positive potentials than 0.24 V, as in curve 2 in Fig. 1, did not yield any current other than the transfer of H⁺ present in W as the supporting electrolyte.

On addition of TPA to DCE, the voltammogram shown in Fig. 2 (a) was recorded. When the potential was scanned to 0.26 V, ion transfer of AuCl₄⁻ between W and DCE was observed, which is similar to the result in the absence of TPA in DCE shown in Fig. 1. However, when the potential was scanned to 0.5 V, the new positive and negative current features, Iₚ₂, Iₚ₃ and Iₙ₂, at 0.02, 0.36 and −0.2 V, respectively, were observed as seen in Fig. 2(b). The currents depended on the number of scans. The black curve of the voltammogram is the 1st scan, and the dotted line is the 10th scan. Iₚ₁ and Iₙ₁, corresponding to the transfer of AuCl₄⁻ between W and DCE, decreased with successive potential scans, while, Iₚ₂, Iₚ₃ and Iₙ₂ increased with repeated potential scanning.

In order to distinguish between ion and electron transfer reactions at Iₚ₂, Iₚ₃ and Iₙ₂, electrochemical measurement where the W and DCE phases are separated by a solid electrode [35,36] was carried out as shown in Fig. 3. Here, glassy carbon and platinum wire electrode were used in W and DCE, respectively to connect both phases. Positive and negative current were observed at 0.45 and −0.3 V, corresponding to electron transfer processes: on the basis of the reduction potentials of the Au complex and the TPA (vide infra), these processes are the electrodeposition and stripping of Au as shown in Fig. 4. From the second scan, another current feature corresponding to the formation of the second layer on the Au deposit was observed at 0.26 V, i.e., deposition on the carbon surface give rise to two peaks, on the initial scan a high potential peak (0.45 V) is seen due to the relatively unfavorable energetics of metal deposition on carbon [38]. These peak potentials correlate well with those of the voltammogram recorded at the W/DCE interface (Fig. 2(b)) and therefore suggest that processes Iₚ₂ and Iₙ₂ correspond to Au deposition and stripping, respectively. Furthermore, Fig. 4 shows typical features of deposition of a metal at the solid electrode, with a cross-over in the current on the first reduction cycle due to nucleation [17,24,37]. Note that the lower potential deposition peak seen in the bipolar case is not apparent at the W/DCE interface, suggesting it is either obscured by the ion transfer current (Iₚ₁/Iₙ₁) or Au deposition is occurring more slowly. The latter suggestion may be supported by the lack of “nucleation loop” seen at the W/DCE interface. Consequently, the AuCl₄⁻ is
Ions -0.

Figure 5 shows the voltammogram recorded at the micro-interface under the same condition as the macro-interface, Fig. 2, except for the concentration of supporting electrolyte in DCE. In the absence of TPA in DCE, negative current corresponding to the transfer of AuCl4− from W to DCE was observed as in curve 1 in Fig. 1. The diffusion coefficient can be calculated from the following equation [31]:

\[ I_{SS} = 4\pi D W r W \]  

(4)

where \( I_{SS} \), \( z \), \( F \), \( D \), \( r \) and \( c_W \) are the steady state plateau current, the charge number involved in the reaction, the Faraday constant, the diffusion coefficient of the ion in W, the entrance (W side) radius and the concentration of the ion in the bulk of W, respectively. The \( D \) calculated (8.3 x 10^-6 cm^2 s^-1) is similar to that calculated at the macro interface (7.9 x 10^-6 cm^2 s^-1). In the presence of TPA in DCE, in addition to the negative current corresponding to the transfer of AuCl4−, a positive current was observed as shown in Fig. 5. The positive current indicates an electron transfer from DCE to W. Here, the shape of the voltammogram did not change with the number of scans. However it was found that the positive current on the forward scan was different from that on the backward scan, whereas minimal hysteresis was seen in the negative current region, corresponding to the transfer of AuCl4−. This suggests that the reaction associated with the positive current is associated with the nucleation of the Au particles. The data is re-plotted as current normalized for AuCl4− concentration. This reveals a decrease in hysteresis as concentration increase, indicating the increased ease of nucleation. The limiting current of the positive process is about twice that of the monovalent AuCl4− ion transfer (see insert in Fig. 5). This ratio of positive to negative current is consistent with a three-electron reduction of Au, coupled to the transfer of AuCl4− from W to DCE.

Table 2 shows the standard potentials, \( \Delta E^0 \),s, of the TPA+/TPA couple in DCE, and the aqueous AuCl4−/Au, AuCl2−/Au and AuCl4−/AuCl2− couples [39]. The oxidation of TPA was investigated voltammetrically and found to give a reversible voltammogram in DCE. The standard electron transfer potential can be calculated from the difference in the standard potentials of TPA+/TPA in DCE and the AuCl4−/Au couple in W (0.008 V). Here, \( \Delta E^0 \)s obtained on the SSE or NHE scales are converted into those with respect to TPhE at the W/DCE interface [40]. Although the electron transfer reaction was irreversible, the mid-point potential under the condition of Fig. 2(b) was estimated to be approximately 0.07 V, which indicates the electron transfer reaction overlaps with the transfer of AuCl4− ion between W and DCE.

3.1.2. Voltammetry of Au deposition using AuCl4− dissolved in DCE

Before the measurement of the voltammogram in the absence of TPA, a voltammogram in the absence of TPA was recorded as shown in Fig. 6(a). The mid-point potential determined from the potentials at the positive and negative currents at \( I_{p1} \) and \( I_{n1} \) in Fig. 6 agreed with that obtained in Fig. 1 and reported previously [4,5,7]. The electrochemical reaction between W and DCE containing AuCl4− and TPA was thus investigated for the case of AuCl4− initially dissolved in DCE. There is no homogeneous reaction between AuCl4− and TPA because of the strong solvent dependence of the reduction potential of the former [7,41]. Specifically, the halide loss associated with AuCl4− reduction means the AuCl4−/Au(0) reduction potential is lowered by ca. 2 V. The cyclic voltammograms changed depending on the number of scans as shown in Fig. 6(b). On scanning from ~0.15 V, a clear transfer of

![Table 2](image)

| Table 2 | Standard potential of each redox couple in W or DCE and standard ion transfer potential between W and DCE. |
|---------|---------------------------------------------------------------------------------------------------------------|
| Redox couple | \( \Delta E^0 \) vs. TPhE / V | Ions | \( \Delta W \) vs. TPhE / V |
|------------|-------------------------------------------------|-----|-----------------|
| TPA/TPA+ in DCE | 0.81 | AuCl4− | 0.115 |
| AuCl4−/Au in W | 0.802 | AuCl4− | 0.026 |
| AuCl2−/Au in W | 0.954 | AuCl4− | 0.73 |
| AuCl4−/AuCl2− in W | 0.73 | AuCl4− | 0.73 |

\( ^\text{a} \) Converted from SSE or NHE, \( ^\text{b} \) ref [39].

![Fig. 5](image)

Fig. 5. Charge transfer voltammogram at the micro-interface between AuCl4− in W and TPA in DCE (Cell 3). Curves 1 to 5 are 0, 0.1, 0.2, and 0.4 mM AuCl4−. Scan rate: 10 mV s−1. (a) absence of TPA, cell 4 (b) presence of TPA (0 mM, Cell 5): Black line; 1st scan, gray lines; 2nd to 4th scans, dotted line; 5th scan.

![Fig. 6](image)

Fig. 6. Ion transfer voltammogram of AuCl4− at the macro-interface between W and AuCl4− in DCE, i.e. AuCl4− initially in DCE phase. Scan rate: 10 mV s−1. (a) absence of TPA, cell 4 (b) presence of TPA (0 mM, Cell 5): Black line; 1st scan, gray lines; 2nd to 4th scans, dotted line; 5th scan.
AuCl$_4$ between W and DCE was observed, which gave a different second voltammogram from that measured when dissolving AuCl$_4$ into W instead of DCE (Fig. 2(b)). From the second scan, positive and negative current peaks were observed at 0.35 V and −0.2 V, corresponding to the electron transfer for the redox equilibrium between AuCl$_4$ and Au(0). Those potentials are close to those obtained in the analogous cell where AuCl$_4$ was initially present in W (Fig. 2(b)). However, the electron transfer current at 0.35 V for the deposition of Au(0) in Fig. 6(b) is clearly higher than that in Fig. 2(b), which must reflect the difference of solvation of the AuCl$_4$ transferred from DCE compared to those initially present in W. AuCl$_4$ transferring from DCE to W would be immediately reduced to Au(0) at the interface by TPA in DCE, based on the potentials reported in Table 2. By scanning 10 times, the current for the transfer of AuCl$_4$, as well as that for the electron transfer, decreased as a result of the irreversible deposition reaction.

3.1.3. Charge transfer voltammetry between W and DCE containing AuCl$_{2}^-$ and TPA

Cyclic voltammograms were measured for the transfer of AuCl$_{2}^-$ between W and DCE as shown in Fig. 7(a). Interestingly, in spite of conventional wisdom suggesting AuCl$_{2}^-$ should disproportionate rapidly in aqueous solution [42], a reversible voltammogram for the transfer of AuCl$_{2}^-$ from W to DCE was observed (Eq. (5)).

\[
\text{AuCl}_{2}^- \text{(W)} \rightleftharpoons \text{AuCl}_{2}^- \text{(DCE)}
\]  

In the presence of TPA in DCE, voltammograms such as that shown in Fig. 7(b) were recorded. Again because of the solvation effects on reduction [7], AuCl$_{2}^-$ did not react spontaneously with TPA in DCE. In addition to the AuCl$_{2}^-$ transfer peaks at 0.08 V, new voltammetric features were observed at 0.2 V on the first scan, with a small negative current seen at −0.2 V. The new features were observed to grow at the expense of the AuCl$_{2}^-$ transfer peaks and are attributed to Au deposition and stripping at the W/DCE interface:

\[
\text{AuCl}_{2}^- \text{(W)} + \text{TPA}^{+} \text{(DCE)} = \text{Au} + \text{TPA}^- \text{(DCE)} + 2\text{Cl}^- \text{(W)}
\]  

The chemical behavior of AuCl$_{2}^-$ in the presence of TPA is similar to that of AuCl$_4^-$ except that the reversible ion transfer peak ($i_{p1}$) is smaller in the AuCl$_{2}^-$ case, and the electron transfer peak ($i_{p2}$) is enhanced, indicating the higher reactivity of AuCl$_{2}^-$. After electrolysis at 0.3 V for 2 hours, particle deposition was observed via TEM.

3.2. Effect of electrolysis conditions on Au nanoparticle formation at the liquid/liquid interface

The electrochemical deposition conditions were varied to determine if control over the nanoparticles’ mean size and/or density occurred on changing the applied potential ($E_{\text{app}}$) and electrolysis time ($t_{\text{app}}$). Experimental conditions are summarized in Table 3. In this study, W containing 10 mM HCl and DCE containing 0.5 mM TOA$^+$ AuCl$_{4}^-$, 20 mM TPA and 10 mM TOA$^+$ TFPB$^-$ (Cell S) was employed. The TOA$^+$ can act as a capping agent for the Au deposit [28].

Electrolysis at $E_{\text{app}} = 0.21$ V and $t_{\text{app}} = 30$ min produced particles in the size range 3–7 nm as shown in Fig. 8 (a). However, the total amount of particles was much lower than formed under the other conditions employed, although a significant deposition current was observed at the potential in Fig. 6(b). $E_{\text{app}} = 0.26$ V and $t_{\text{app}} = 30$ min, gave many 3 nm diameter particles in addition to the lesser number of particles in the 2–7 nm range shown in Fig. 8(b). At $E_{\text{app}} = 0.31$ V, particles of 3–5 nm diameter were mainly observed (Fig. 8 (c)). The average size of those particles at $E_{\text{app}} = 0.31$ V seemed to be larger than $E_{\text{app}} = 0.21$ and 0.26 V. Particles around 50 nm in diameter were observed at $E_{\text{app}} = 0.36$ V and $t_{\text{app}} = 30$ min in addition to the ca. 10 nm diameter particles. The size of particles produced was not closely correlated with the applied potential, although there was a tendency to form larger particles, at more positive potential. The ex-situ nature of the TEM analysis makes comparative evaluation of particle number difficult but the exponential increase in current with potential in the potential range of Fig. 6(b) [compare with Fig. 5] therefore suggests that the main change with potential is likely with respect to the number of particles formed. Table 3 gives the charge passed for the different $E_{\text{app}}$ and $t_{\text{app}}$. No particles were observed from TEM samples obtained at potentials below the onset of $I_{p3}$ in Fig. 6(b) (specifically $E_{\text{app}} = 0.16$ V and $t_{\text{app}} = 30$ min). Finally, longer term electrolysis was carried out using $E_{\text{app}} = 0.16$ and 0.21 V for $t_{\text{app}} = 60$ min. Fig. 8 (d) shows the result from $E_{\text{app}} = 0.21$ V and $t_{\text{app}} = 60$ min. Larger particles having diameter in the range 4–8 nm were observed compared with those formed at the same potential and $t_{\text{app}} = 30$ min. Moreover there was evidence of particle aggregation in the case of the longer $t_{\text{app}}$ experiments (10–15 min). Consequently, synthesis of particle with diameters less than 10 nm requires $E_{\text{app}} = 0.21–0.31$ V and $t_{\text{app}} = 30$ min under the experimental conditions employed here.

Table 3: Electrochemical deposition experimental by changing applied potential ($E_{\text{app}}$) and duration time ($t_{\text{app}}$) under the condition of Cell S. Q is the charge.

| Batch No. | $E_{\text{app}}$ vs. TPHE / V | $t_{\text{app}}$/min | Q /μC |
|----------|-----------------------------|---------------------|-------|
| 1        | 0.16                        | 30                  | 6.76  |
| 2        | 0.21                        | 30                  | 12.3  |
| 3        | 0.25                        | 30                  | 18.7  |
| 4        | 0.31                        | 30                  | 27.1  |
| 5        | 0.16                        | 60                  | 12.1  |
| 6        | 0.21                        | 60                  | 22.4  |

Fig. 7. Ion transfer voltammmogram of AuCl$_4$ at the macro-interface between W and AuCl$_4$ in DCE. Scan rate: 10 mV s$^{-1}$. (a) in the absence of TPA (Cell 6); (b) with TPA in DCE (Cell 7); black line: 1st scan, gray line: 2nd to 9th scans, dotted line: 10th scan.
4. Conclusions

It has been found that Au deposit was formed at the interface from the simultaneous reduction of AuCl$_4^-$ or AuCl$_2^-$ in W and concomitant oxidation of TPA as a reductant in DCE. Ion transfer voltammetry indicated that AuCl$_2^-$ is stable, at least on the second timescale, in aqueous solution. The formation of Au nanoparticle with diameters less than 10 nm was more sensitive to time of electrolysis than the applied potential.

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