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Journal of Experimental Nanoscience

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t716100757>

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Online publication date: 08 February 2010

To cite this Article Zhu, Yong-Chun, Kuang, Ya-Wen and Meng, Xiang-Yu(2010) 'The assembling kinetics of silver nanoparticles on supported methyl silicone membrane by cyclic voltammetry', *Journal of Experimental Nanoscience*, 5: 1, 1 – 9

To link to this Article: DOI: 10.1080/17458080903115353

URL: <http://dx.doi.org/10.1080/17458080903115353>

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The assembling kinetics of silver nanoparticles on supported methyl silicone membrane by cyclic voltammetry

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(Received 20 December 2008; final version received 13 June 2009)

The chemically synthesised silver nanoparticles in colloidal solution were assembled on the methyl silicone oil membrane supported on the graphite–epoxy composite electrode, and monitored by cyclic voltammetry. The assembling kinetics follows a diffusion-controlled Brownian movements of the nanoparticles with a Weibull function and a rate constant of 0.02548/min. The assembled silver nanoparticles undergo a self reorganisation process in the methyl silicone oil membrane in contact with 0.1 M KCl electrolyte solution due to the interaction of silver atoms with chloride ions, and follows another Weibull function with a rate constant of 0.0467/min. The reorganised silver nanoparticles in methyl silicone oil membrane show a surface-controlled electrochemical behaviour.

Keywords: silver nanoparticle; methyl silicone oil membrane; assembly dynamics; self reorganisation; cyclic voltammetry

1. Introduction

Nanoparticles attract more and more people's attention due to their optical, electrical and structural properties [1]. The capture of nanoparticles on a variety of substrates offers a new way to fabricate new nanomaterials and nanodevices with novel or enhanced physical and chemical properties and applications [2–4], such as the self-organisation or self-assemblies of gold and silver nanoparticles at solid–liquid surfaces [5, 6], and liquid–liquid interfaces, especially oil–water interfaces, which offer potential applications such as design and synthesis of nanodevices [7], drug release [8], nanoparticle stabilisation [9], integration or separation of biomolecules [10]. Most nanoparticles were synthesised in a solution such as colloidal solution, and how to manipulate the nanoparticles into an array pattern is very important process for future applications. One simple and powerful way is the thin liquid membrane extraction of the nanoparticles due to the interactions of nanoparticles with organic molecules, such as electrostatic interaction, hydrophilic or hydrophobic interactions [11–13]. During the assembly membrane formation, the nanoparticles form some array patterns such as Frank–van-der Merwe (FM) [14], Volmer–Weber (VW) [15], Stranski–Krastanov (SK) [16], known as self-assemblies [17–19]. Some surface sensitive

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methods [20–22], and surface plasma resonance spectrometry [23] can be used to monitor the process and the pattern formation can be visualised by atomic force microscopy [24] and optical microscopes [25].

Electrochemistry as a surface sensitive method especially in the electron and ion transfer properties studies has been used in the study of the self-assembly membrane of single molecular layer properties [26,27]. Metal nanoparticles, such as silver and copper have very good electrochemical redox properties. Aveyard et al. [28] described an interesting method to trap nanoparticles into a water miscible liquid with higher viscosity to build up a 2D lattice. If the liquid membrane is supported on a graphite–epoxy composite electrode (GECE) surface, then the trapping process can be monitored by electrochemical method. In this work, the assembling kinetics of silver nanoparticles on methyl silicone oil membrane from colloidal solution was monitored by an electrochemical method. Some useful information about dynamics of the assembling process and the following self reorganising process in contact with chloride solution as well as the electrochemical properties of the trapped silver nanoparticles were monitored.

2. Experimental

2.1. Reagents and instruments

Methyl silicone oil, analytically pure, was directly used without further treatment. KNO_3 , KCl and other reagents, all analytically pure, were prepared into 1.0 mol/L aqueous solution. AgNO_3 , NaBH_4 , analytically pure, were prepared into 2.0 and 1.00 mmol/L aqueous solution before use. All solutions were prepared with ultra-pure water from MilliQ (18.2 M Ω). All the solutions were pre-deaerated with high-pure nitrogen gas for 20 min before carrying out electrochemical experiments.

The electrochemical experiments were carried out with a CHI620b electrochemical equipment (made in USA). A conventional three-electrode cell was used with a piece of spiral platinum wire as counter electrode, a homemade graphite–epoxy solid electrode (GESE in a glass tube as a working electrode (geometry area about 0.12 cm²) and a saturated calomel electrode (SCE) as a reference electrode. All potentials reported here are with respect to this reference electrode.

The GECE as a three-phase (insulator/solution/electrode) electrode [29] was polished with 360#, 600# 800#, 1000# sandpapers and glassine paper sequentially, uniformly coated with a thin layer of methyl silicone oil with glass bar and slightly polished again with a glassine paper, by hand to keep the oil layer uniform and thin.

2.2. Electrochemical experimental procedures

2.2.1. Monitoring of the assembling process

The methyl silicone oil coated electrode was immersed in the silver colloidal solution vertically with the electrode surface facing downwards including 0.10 M KNO_3 as the electrolyte to perform cyclic voltammetric experiments with the initial potential of -0.30 V, final potential of 0.40 V, quiet time of 30 s at a scan rate of 50 mV/s, until the anodic peak current reached the plateau state.

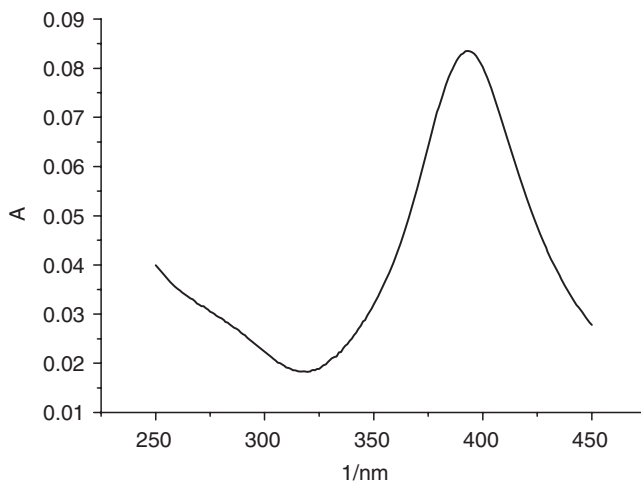


Figure 1. UV-visible adsorption spectrum of colloidal silver solution.

2.2.2. Monitoring the reorganisation process

After the oil membrane traps the silver nanoparticles reaching the saturated state, the electrode was carefully washed with ultra-pure water, and then immersed in the 0.10 M KCl electrode solution. The cyclic voltammetric experiments were performed in the potential range $-0.30 \sim -0.40$ V at 50 mV/s scan rate with a quiet time of 30 s continuously, until the anodic peak current reached the stable value.

2.3. Preparation and characteristics of colloidal silver solution

The silver colloidal solution was chemically prepared with 25 mL newly prepared 0.01 M NaBH_4 solution in 100 mL beaker, added 15 mL newly prepared 1.0 mmol/L AgNO_3 solution with magnetic stirring. A bright yellow colloidal solution was obtained. The UV-Visible spectrum of the colloidal solution was obtained as shown in Figure 1 with the maximum adsorption wavelength $\lambda = 392$ nm, which indicates that the colloidal solution including silver nanoparticles [23] with a particle size of about 5 nm in diameter.

3. Results and discussion

3.1. Assembling dynamics of silver nanoparticles on liquid membrane

The cyclic voltammograms for the different assembling times are shown in Figure 2(a). In the first scan, the CV curve shows only one complete irreversible anodic peak located at 0.287 V without cathodic peak. In the second scan, there are two anodic peaks located at 0.167 and 0.313 V, respectively, while in the returned scan, only one cathodic peak is located at -0.149 V. With the trapping progress going on, the two anodic peaks combined together into one anodic peak located at 0.172 V, which shifts to negative direction, and is finally located at 0.162 V, while the cathodic peak shifts to negative direction, and is finally located at -0.173 V. The redox peak currents reach the plateau at the end of the process, the CVs during the trapping process as shown in Figure 2(a). The anodic current increased

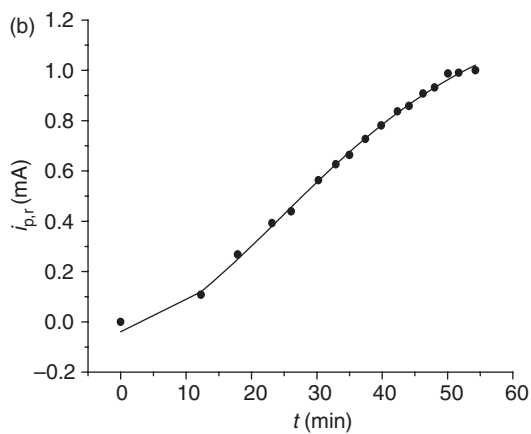
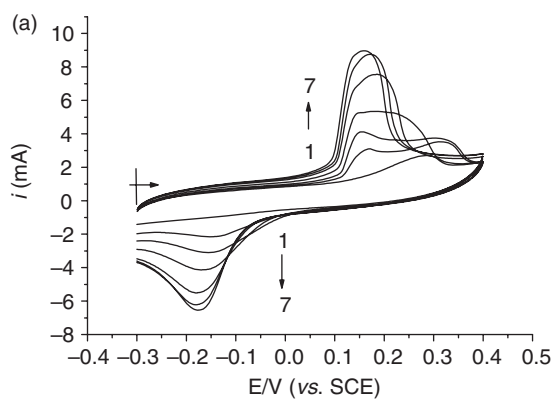


Figure 2. The CVs (a) and the relationship of anodic peak current with assembling time (b) of silver nanoparticles in the liquid membrane trapping process and (c) is the metallic microscopic image of the silver nanoparticles trapped in methyl silicone oil membrane supported on glass plate (Olympus, made in Japan, magnification $\times 1200$). Scan rate: 50 mV/s; t (min): 1, 0; 2, 12.3; 3, 17.9; 4, 30.2; 5, 39.8; 6, 50.0; 7, 54.3.

from the initial value of 1.261 to 7.176 μA at 48 min. The current was normalised as $i_{\text{pc,R}} = (i_{\text{p,t}} - i_{\text{pa,0}})/(i_{\text{p,\infty}} - i_{\text{pa,0}})$, and plotted against assembling time, a Weibull function was obtained as shown in Figure 2(b) with a regression equation of $i_{\text{pa,R}} = 1.248 - 1.287 \exp(-0.001686 t^{1.74})$, $R = 0.999$, $\text{SD} = 0.01353$. The characteristic assembling time is 39.24 min, the first-order apparent assembling rate constant is calculated as 0.02548/min. The Weibull modulus, $1 < m = 1.74 < 3$, belongs to the normal distribution model [30].

The methyl silicone oil has higher viscosity. When the silver nanoparticles diffuse into the oil membrane, they are captured and they form an assembly membrane with two-dimensional pattern [23] because of the charges of the same sign of the silver nanoparticles, the metallic microscopic image is shown in Figure 2(c). The peak current is proportional to the $(4Dt)^{1/2}$. The anodic peak current plotted against the square root of assembling time is a straight line with the regression equation $i_{\text{p}}(\mu\text{A}) = -0.79351 + 0.03211t^{1/2}$ ($R = 0.9983$, $\text{SD} = 0.01647$), $D = 2.578 \times 10^{-4} \text{ cm}^2/\text{s}$. This indicates diffusion of nanoparticles according to the Brownian movements in colloidal solution.

The anodic peak current is proportional to scan rate with the regression equation $i_{\text{pa}} = -0.10461 + 0.11905 v$ ($R = 0.9977$, $\text{SD} = 0.03826$), which indicates a surface-controlled process, and means that the silver nanoparticles are assembled on the methyl silicone oil membrane at the electrode surface. The cathodic peak current shows the surface- and diffusion-controlled processes with a regression equation $i_{\text{pc}} = -0.1527 + 0.08204 v^{1/2} + 0.00278 v$ ($R = 0.9977$, $\text{SD} = 0.03595$). This result indicates that the reduction currents are partly from bulk silver colloidal solution and partly from the oxidation of silver nanoparticles assembled at the active sites of the electrode surface.

3.2. Reorganisation dynamics of the assembled silver nanoparticles in contact with KCl electrolyte solution

The electrode with the assembled silver nanoparticle membrane was immersed in a 0.10 M KCl electrolyte solution and was monitored by cyclic voltammetry (CV). The CVs are shown in Figure 3(a). In comparison with Figure 2(a), the oxidation peak becomes sharp, and peak current increases with time from the initial value of 54.93 to 134.7 μA at 48 min, and reduction peak current increases from 14.3 to 45.9 μA at 48 min. This phenomenon indicates that the assembled silver nanoparticle membrane undergoes a reorganisation process in contact with 0.1 M KCl electrolyte solution [31], and this increases the order of the membrane and electrochemical activity.

The anodic current is normalised as above. The plot of normalised anodic peak current against reorganisation time is a sigmoidal curve (Figure 3b) with the regression equation of Weibull function [30] of $i_{\text{pa,R}} = 1.3695 - 1.366 \exp(-0.00491t^{1.735})$, $R = 0.998$, $\text{SD} = 0.0211$. The characteristic time of the self reorganisation was obtained as 21.4 min with the first-order self reorganisation constant of 0.0467/min. The self reorganisation process is mainly due to the replacement of KNO_3 electrolyte with KCl. In KCl electrolyte solution, the chloride anion precipitates or coordinates with silver atoms and cation at the nanoparticle surface produced during the electrochemical oxidation process. So the assembled silver nanoparticle on the oil membrane will reorganise with chloride ions and forms a self-organised layer, which is more stable and favourable for the redox of silver. The oxidation peak negatively shifts to 0.043 from 0.162V, while the reduction peak shifts negatively to -0.243V from -0.173 in KNO_3 electrolyte solution. The coordination

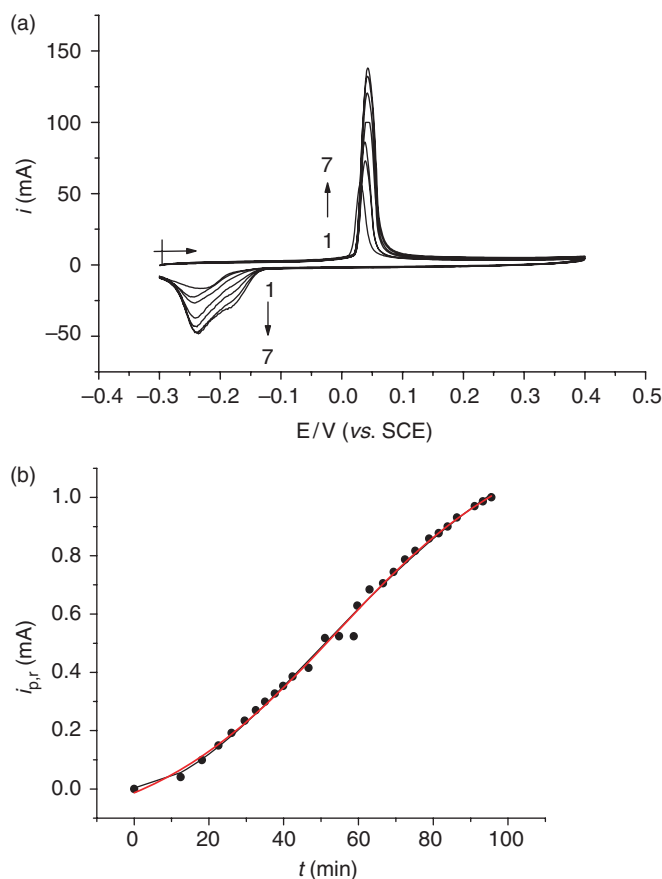


Figure 3. The CVs (a) and the relationship of normalised peak current with time (b) of silver nanoparticles in the re-organisation process in contact with 0.1 mol/L KCl solution. Scan rate: 50 mV/s; t (min): 1, 0; 2, 6.5; 3, 14.6; 4, 22.7; 5, 30.7; 6, 38.9; 7, 45.4.

constants of silver cation with chloride ion, $\log \beta_1$, can be found from general handbooks as $i = 1-4$: 3.04, 5.04, 5.04, 5.30, respectively. The redox reactions of silver nanoparticles are irreversible process; there are no equilibrium potentials, so the reduction potential and the oxidation potential can be separately calculated according to Nernstian's equation. In the oxidation process, the silver atom at the silver nanoparticle surface coordinates with one chloride ion, the anodic potential is calculated as

$$\phi_{\text{re,nano}} = -0.05916 \log(K_{f1}) - 0.059161 \log(c_{\text{Cl}^-}) + 0.05916 \log[\text{AgCl}]/[\text{AgCl}]^- \quad (1)$$

$\phi_{\text{re,nano}} = -0.162 - 0.180 + 0.05916 = 0.041\text{V}$, which is in accordance with the experimental value, $E_{\text{p,a}} = 0.040\text{V}$. In reduction process, the oxidised silver ion coordinates with four chloride ions and forms a complex



The cathodic peak potential can be calculated as

$$\begin{aligned} \phi_{\text{ox,nano}} = \phi_{(\text{ox,nano})}^0 - 0.05916 \log(K_{f4}) - 4 \times 0.059161 \log(c_{\text{Cl}^-}) \\ + 0.05916 \log[\text{AgCl}]/[\text{AgCl}]^- \end{aligned} \quad (3)$$

$\phi_{\text{ox,nano}} = -0.173 - 0.313 + 0.237 = -0.249$ V, which is very similar to the experimental value $E_{\text{pc}} = -0.243$ V.

Self-organisation of the assembled membrane is a new phenomenon that occurs in contact with chloride solution [31], which offers a new chance for the nanoparticle applications.

3.3. Electrochemical properties of the self reorganised silver nanoparticles

After the membrane becomes stable, the CV experiments were performed with different scan rates. The anodic and cathodic peak currents are proportional to the scan rate with the regression equations $i_{\text{pa}} = -62.06 + 22.86 v$, $R = 0.9983$, $\text{SD} = 5.70$; $i_{\text{pc}} = 0.2464 + 0.6099 v$, $R = 0.9996$, $\text{SD} = 1.849$, which indicates that the silver nanoparticles are located at the electrode surface. The anodic peak potential shifts positively with the square root of scan rate, $E_{\text{pa}} = 0.001328 + 0.0033 v^{1/2}$, $R = 0.998$, $\text{SD} = 0.0012$, but the cathodic peak potential shifts negatively with the quarter root of scan rate, $E_{\text{pc}} = -0.1604 - 0.02559 v^{1/4}$, $R = 0.9805$, $\text{SD} = 0.0047$, which follows a spherical particle growth model [32] that means the nanoparticle grows spherically.

4. Conclusions

In summary, the colloidal silver nanoparticles were assembled onto the methyl silicone oil membrane supported on GECE in 2D silver nanoparticle array pattern. The CV is a powerful method for monitoring the assembling process, which follows the Weibull distribution functions controlled by diffusion. The assembled silver nanoparticles undergo a self reorganisation process in contact with 0.10 M KCl solution and shows a spherical particle growth process in its reduction process in the liquid membrane.

Acknowledgements

The authors would like to acknowledge the financial support of the Chinese National Science Foundation (20875063), Liaoning Education Minister Foundation (2004-c022), Shenyang Sciences and Technology Bureau Foundation (2007-GX-32) and National Key Laboratory on Electroanalytical Chemistry Foundation (2006-06).

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