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The preparation of a gold nanoparticle monolayer on the surface of a polymer inclusion membrane using EDTA as the reducing agent

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ABSTRACT

A polymer inclusion membrane (PIM) consisting of Aliquat 336 (20% m/m), 1-dodecanol (10% m/m) and PVC (70% m/m) has been used as a template to prepare gold nanoparticles (Au NPs). $AuCl_4^-$ has been extracted into the membrane via ion-exchange and has been subsequently reduced by L-ascorbic acid, tri-sodium citrate, $NaBH_4$ or EDTA to form Au NPs. EDTA at pH 6.0 has been shown to be an effective reducing agent capable of forming a uniform monolayer of Au NPs of average size 20 nm on the surface of the membrane. The other reagents have formed Au NPs of sizes depending on the reagent type and these have been embedded in the bulk of the membrane and not concentrated at the surface.

The main factors influencing the formation of the surface Au NPs when EDTA is used as the reducing agent have been studied. A 24 h membrane exposure to the EDTA solution has ensured complete surface coverage with Au NPs. It has been observed that as the concentration of EDTA, the solution temperature and shaking rate increase, the size of Au NPs decreases. Therefore, these factors can be used to control the size of Au NPs on the membrane surface.

The coated with Au NPs membranes are expected to be of interest in optical sensing and catalytic applications.

1. Introduction

During the past two decades, there has been a rapid growth in nanoscience with many important applications emerging [1]. Gold nanoparticles (Au NPs), in particular, have become a popular topic for research due to their unique photonic, electronic, magnetic and catalytic properties [2,3]. Au NPs of different size and structure can be prepared using a wide variety of methods which result in changes in their appearance and properties. This has led to many important applications (e.g. novel biomedical imaging techniques and therapies [1–4]; sensor development for detecting biological molecules [5–8] and heavy metals ions [9,10]; catalytic surfaces for various reactions [11–14]). In general, there are two main processes for Au NPs synthesis, namely, linear-template methods and template-free self-assembly methods [2]. Linear-template methods involve the use of templates to grow Au NPs in the presence of a suitable reducing reagent. The templates used range from linear polymers, biomolecules (e.g. DNA and proteins), inorganic nanowires and nanotubes, and step edges on solid substrates (e.g. electrodepositing of NPs on solid substrates) [3,8]. The preparation of Au NPs on linear polymers such as Nafion, poly(vinyl chloride) (PVC) and cellulose triacetate (CTA) has been studied widely [8,9,13,15–17].

In recent years, processes based on the use of polymer inclusion membranes (PIMs) for selective separation of both metallic and non-metallic species have attracted considerable attention [18–31]. They have many advantages over other processes as they use lower amounts of solvents than solvent extraction and the membrane systems are usually compact and robust, enabling them to be easily implemented in existing industrial processes. These membranes are formed by casting a solution containing an extractant, a plasticizer and/or modifier and a base polymer dissolved in a volatile solvent such as tetrahydrofuran (THF) and allowing the solvent to evaporate. The resulting membrane is transparent and visually homogeneous and has a number of advantages over the other types of liquid membrane (e.g. supported liquid membranes, bulk liquid membranes and emulsion liquid membranes [32]), particularly in terms of stability. The extractant or carrier, usually a complexing agent or an ion-exchanger, is an essential component for metal extraction [19]. A plasticizer (e.g. 2-nitrophenyloctyl ether (2-NPOE)) and/or modifier (e.g. 1-dodecanol) is often added to the membrane composition to increase the membrane softness, flexibility and compatibility of the membrane components and also to increase the diffusive flux within the polymer matrix [19,20].

Argiropoulos et al. [18] have used a PIM containing Aliquat 336 immobilized in PVC in the extraction of gold(III) from hydrochloric

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acid solutions. The proposed mechanism for the extraction involves an ion-exchange reaction between the chloride ion of Aliquat 336 and the tetrachloroaurate(III) anion ($AuCl_4^-$) in solution. The PIM was found to be highly selective for Au(III) even in the presence of a high concentration of copper. More recently, we have revisited this extraction system with a view to optimizing the membrane composition in order to obtain higher membrane diffusivity and stability. This work established the optimum membrane composition for the extraction of Au(III) to be 20%(w/w) Aliquat 336, 10% (w/w) 1-dodecanol and 70% (w/w) PVC [33].

Kumar et al. recently published a paper in which they described the synthesis of Au NPs using a PIM containing Aliquat 336 immobilized in a CTA polymer matrix with dioctyl phthalate (DOP) as plasticizer [15,34]. Firstly, Au(III) was extracted into the membrane from chloride solutions and was then reacted with a $NaBH_4$ solution. This resulted in the formation of metallic Au NPs with an average size of 10 nm distributed throughout the bulk of the membrane.

Thus, it was of interest to study this approach for making Au NPs using our Au(III) loaded PVC-Aliquat 336 PIMs. This study compares the effect of a number of reducing agents (L-ascorbic acid, tri-sodium citrate, $NaBH_4$, and ethylenediaminetetraacetic acid (EDTA)) on the formation of Au NPs. The research focuses on the use of EDTA which was described recently by Wang et al. as a reagent capable of reducing the $AuCl_4^-$ ion in its aqueous solutions to metallic gold in the form gold nanocrystals [35].

2. Experimental

2.1. Chemicals

Aliquat 336 (Aldrich, a mixture of quaternary ammonium chlorides), high molecular weight powdered PVC (Fluka), cellulose triacetate (CTA) (Aldrich), 1-dodecanol (Aldrich), dichloromethane (Lab-scan, Australia), and tetrahydrofuran (Chem-supply, Australia) were used as received. Au(III) calibration standards were made from a 1000 mg L^{-1} Au(III) standard solution (BDH Spectrosol).

Au(III) solutions for membrane extraction were prepared from $HAuCl_4$ (Aldrich) dissolved in 2.5 mol L^{-1} HCl (Chem-supply, Australia). Aqueous solutions (0.10 mol L^{-1}) of L-ascorbic acid (Sigma), tri-sodium citrate (Chem-supply, Australia) and sodium borohydride (Ajax Finechem, Australia) were used for the reduction of Au(III). EDTA solutions were prepared from the disodium salt (Fison) and the pH was adjusted with 0.10 mol L^{-1} HCl or NaOH (Chem-supply, Australia).

The determination of the amount of EDTA extracted by PIMs was carried out by reaction with $Zn(PAR)_2$ solution (2.0×10^{-3} mol L^{-1}) prepared by dissolving $ZnCl_2$ (Unilab, Australia) and 4-(2-pyridylazo) resorcinol (PAR) (Aldrich) in borate buffer. The borate buffer at pH 9.3 was prepared by mixing a 5.0×10^{-2} mol L^{-1} solution of $Na_2B_4O_7$ (Chem-supply, Australia) and a 0.50 mol L^{-1} H_3BO_3 solution (Ajax Finechem, Australia) in a 9:1 ratio by volume [36]. All other chemicals were of analytical reagent grade. Deionized water (18 MΩ cm, Millipore, Synergy 185, France) was used for the preparation of all aqueous solutions.

2.2. Instrumentation

The concentration of Au(III) in its aqueous solutions was determined by atomic absorption spectrometry (AAS, Hitachi Z-2000 Series Polarized Zeeman atomic absorption spectrometer, Japan). The concentration of EDTA in its aqueous solutions was determined by visible spectrophotometry (Libra S12, Biochrom, UK) using the decrease in absorbance of the $Zn(PAR)_2$ complex at 491 nm.

The temperature controlled extraction experiments were conducted in conical flasks positioned in a thermostated orbital mixer incubator (Model OM11, Ratek) for temperatures of 20 °C and above and on a platform orbital mixer (Model OM6, Ratek) located in a commercial refrigerator (CLEGG, temperature controller E5CN, OMRON) for temperatures below 20 °C.

Optical microscopy and membrane thickness measurements were conducted with a Motic SMZ-140 stereo microscope (Motic, China) with 60× magnification in combination with a MoticCam 1000 microscope camera (Motic, China).

A FEI Quanta 200 F (FEI, USA) scanning electron microscope (SEM) was used for membrane imaging. Measurements were carried out at 20 kV in high vacuum. The resolution for this instrument as stated by the manufacturer is between 1.2 nm and 3.0 nm at 30 kV and 1 kV, respectively. The size of the Au NPs was assessed by Scandium 5.0 software (Olympus Soft Imaging Systems, Japan).

The surface analysis of gold coated PIMs was conducted using an inductively coupled plasma mass spectrometer (ICP-MS) with laser ablation (Model 810, Varian). The presence of EDTA in PIMs was determined by IR spectrometry (Tensor 27, Bruker) equipped with OPUS software.

The UV–Visible spectrum of the optimal membrane containing Au NPs was obtained with a Perkin Elmer Lambda 950 UV–Vis–NIR spectrophotometer with a 150 mm integrating sphere (Lambda 950, Perkin Elmer). Reflectance mode was used as the Au NPs were concentrated on the surface of the membrane which resulted in lack of transparency of the sample.

2.3. Membrane preparation

Aliquat 336 (20% m/m), 1-dodecanol (10% m/m) and PVC or CTA (70% m/m) with a total mass of 400 mg were dissolved in a small volume of THF for PVC or dichloromethane for CTA. The solution (8–10 mL) was poured into a glass ring with a diameter of 7.5 cm, positioned on a flat glass plate. The mixture was covered with a filter paper and a watch glass to allow slow evaporation of the solvent over a 24 h period leaving a transparent and flexible circular membrane. The membrane was removed from the glass plate and cut to size (mass 60 ± 3 mg, diameter 3.5 cm, thickness 50 ± 5 μm).

2.4. Au(III) extraction

Membranes were immersed in 100 mL of 100 mg L^{-1} Au(III) solutions containing 2.5 mol L^{-1} HCl in conical flasks which were shaken under controlled temperature on a platform orbital mixer at 150 rpm. Samples of the Au(III) solution (0.4 mL) were removed at predetermined time intervals throughout the course of the experiment. The samples were diluted to 8 mL with deionized water and the Au(III) concentration was determined by AAS.

2.5. Reduction of Au(III)

Au(III) loaded membranes were immersed in conical flasks containing 100 mL of 0.10 mol L^{-1} solutions of the individual reducing reagents studied. The flasks were shaken on a platform orbital mixer at 150 rpm for a period of 24 h. The membranes were then removed from the solutions, washed with deionized water and allowed to dry in air. A 1 cm × 1 cm square was cut from the centre of each membrane and mounted on a carbon tab (12 mm) with a pin type SEM mount (12.6 mm). The images of the surface and the cross-section of the membrane were captured using SEM. The average size of the Au NPs was determined by averaging the size of 10 different Au NPs from 5 different spots of the membrane measured with Scandium 5.0 software.

The procedure outlined above was used in studying the influence of the experimental reduction conditions (i.e. extent of