



# Polymer inclusion membranes as substrates for controlled *in-situ* gold nanoparticle synthesis

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## ABSTRACT

Poly(vinyl chloride) (PVC)-based polymer inclusion membranes (PIMs) containing the commercial anionic extractant Aliquat 336 and in some cases also 1-dodecanol as plasticizer were used for the fabrication of PIM surface-confined Au nanoparticles (NPs) by reduction of Au(III), extracted into the membranes as the  $[\text{AuCl}_4]^-$  complex. The experimental conditions controlling Au NP size and distribution were studied using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The former technique showed unique NP distributions dependent on the reducing agent used while XRD data were found to be consistent with those obtained by wide-angle X-ray scattering (WAXS) and revealed that the Au crystallite size decreased when the reduction temperature, reduction time, or reducing agent strength were increased.

Conditions for producing PIM supported Au NPs that could be appropriate for chemical sensing or catalytic applications and with an acceptable thermal stability, based on thermogravimetric analysis (TGA) measurements, were established. Loaded to saturation with Au(III) PVC-based PIMs containing 20 wt% Aliquat 336 and 10 wt% 1-dodecanol were found to be suitable for producing dense Au NP layers which could be appropriate for catalytic applications. Partially loaded with Au(III) PVC-based PIMs without a plasticizer and containing 30 wt% Aliquat 336 allowed the fabrication of discrete disperse Au NPs on the membrane surface which could be expected to be suitable for sensing applications.

This study demonstrates that PIMs are attractive low-cost substrates for the synthesis and immobilization of Au NPs of controlled size, density and shape which can potentially be used in catalytic and chemical sensing applications.

## 1. Introduction

Metal nanoparticles (MNPs) have been a particular area of interest within the field of nanoscience with great potential for applications such as chemical sensing or catalysis [1, 2]. For chemical sensing applications, the unique properties exhibited by MNPs differ from those of the bulk material and can be highly sensitive to the surrounding environment [3]. For catalytic applications, MNP catalysts show superior reaction selectivity and surface area to volume ratios in comparison to traditional bulk metal catalysts [4, 5].

One of the challenges in using MNPs for practical applications is immobilizing them on a suitable substrate. Of the common substrates, polymer based supports are convenient, easily available and can often improve NP stability by eliminating problems associated with NP agglomeration [6, 7]. Polymer supported MNPs can be produced *ex situ* by use of colloidal techniques followed by subsequent deposition onto polymer supports [8]. This approach has the advantage of direct

application of the extensive knowledge on solution-based NP synthesis already available in the literature. However, *in-situ* synthesis of MNPs, *i.e.*, synthesizing directly on the substrate, simplifies the process and allows synthesis of MNPs on a range of surfaces that can be coated with the polymer substrate. Towards this end some relatively recent research on the use of polymer inclusion membranes (PIMs) for the synthesis of Au NPs is of particular interest [9–11].

PIMs are hydrophobic films and separation based on these membranes has emerged as an attractive alternative to conventional solvent extraction or separation involving supported liquid membranes [12, 13]. PIMs have been used for the selective extraction of chemical species such as metal ions from aqueous solutions [12–16]. These membranes consist of a base polymer, an extractant (often referred to as carrier) and a plasticizer or modifier as needed. As metal ions can be readily extracted and then subsequently reduced to synthesize MNPs, PIMs can be used for *in-situ* synthesis of MNPs. The utilization of PIMs for such applications has only recently been explored, with initial work

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by Kumar et al. [9] using cellulose triacetate (CTA)-based PIMs. This study was followed by more extensive research by Bonggotgetsakul et al. [10, 17, 18] using poly(vinyl chloride) (PVC)-based PIMs for the synthesis of Au, Ag or Pd NPs predominantly on the membrane surface. This was achieved by selecting reductants which could not be readily extracted into the corresponding membranes from the reductants' solutions. In this case the extracted into the membranes metal cations (Au(III), Ag(I) or Pd(II)) could be reduced only on the corresponding membranes' surfaces where they formed Au, Ag or Pd NPs. The concentration gradient within the membranes, generated in this way, induced diffusional mass transport of metal cations from the interior of the membranes towards their surfaces. The effect of important experimental conditions such as the loading time, determining the extent of membrane loading with metal ions, and the reduction time during which the membrane was exposed to the reductant's solution were investigated. Most recently work by Mora-Tamez et al. [11] explored the use of several different types of membranes including CTA-based PIMs for simultaneous extraction and *in-situ* reduction to produce supported Au NPs. This work also demonstrated that these Au NPs were catalytically active in the reduction of 4-nitrophenol. As cheap, optically transparent, easily handled, simple to produce, plastic-like solids that can concentrate large quantities of metal ions, PIMs have significant potential for surface synthesis and immobilization of MNPs.

The Au NP *in-situ* synthesis occurs entirely on or within the PIM and variations in membrane composition, metal ion loading, and subsequent reduction conditions influence the morphology and size of the supported NPs produced. In order to use this system for practical applications it is necessary to understand the effects of these variations throughout the synthesis process. In the research of Bonggotgetsakul et al. [10, 17, 18] the role of loading temperature, loading time, reduction temperature, reduction time, and reducing agent were preliminarily explored by examining the resulting Au, Ag and Pd NP morphology using scanning electron microscopy (SEM). However, as an initial exploratory approach working within the limitations of SEM for evaluation of particle size, the research mentioned above was unable to establish the appropriate experimental conditions for producing Au NP coated PIMs tailored towards chemical sensing or catalytic applications. Instead past work was only focused on producing surface bound NPs. Furthermore, previous work did not address the correlation between trends in Au NP synthesis on PIMs and Au NP synthesis by traditional solution-based methods.

The purpose of this study was to gain a better understanding how various experimental conditions control the process of Au NP synthesis on PVC-based PIMs by the use of a suite of surface characterization techniques providing complementary information. SEM was heavily utilized for qualitative estimation of Au NP size, as well as evaluation of Au NPs distribution and shape. However, in this study, unlike in previous research, SEM results were complemented with atomic force microscopy (AFM) and X-ray powder diffraction (XRD) analysis, thus significantly improving the reliability of the conclusions made. AFM was explored for comparison to other techniques and showed good agreement with SEM results but was ineffective for dense Au NP layers and rough surfaces. Use of XRD allowed a more systematic evaluation of Au crystallite size across different conditions. As has been noted elsewhere [19] multiple characterization techniques should be utilized in order to understand systems of this complexity. By outlining both the key synthesis parameters and their relative effects on Au crystallite size this study serves as a starting point for selection of appropriate PIM supported Au NPs synthesis conditions towards future applications.

## 2. Experimental

### 2.1. Reagents

All reagents were used as received. Deionized water (18.2 M $\Omega$  cm, Synergy 185, Millipore) was used for the preparation of all aqueous

solutions.

High molecular weight PVC (Sigma-Aldrich) was used as the base-polymer for membrane casting. Aliquat 336 (a mixture of quaternary alkylammonium chlorides, Sigma-Aldrich) with  $\geq 88.5\%$  purity due to the presence of octanol and dodecanol was used for extracting the  $[\text{AuCl}_4]^-$  complex into the PIMs studied. 1-Dodecanol (Sigma-Aldrich,  $\geq 98\%$  purity) was used as a plasticizer for some of the PIMs.

Tetrahydrofuran (THF) (VWR,  $\geq 99.7\%$  purity) was used for preparing the PIM casting solutions.

Gold(III) chloride trihydrate (Sigma-Aldrich,  $\geq 99.9\%$  purity) stock solutions were used for the preparation of the Au(III) feed solutions after appropriate dilution. Nitric acid (70 wt%, Ajax Chemicals) was used in the preparation of Au(III) feed solutions while NaOH (pellets, Chem-supply,  $\geq 97\%$  purity) was used for adjusting the pH of ethylenediaminetetraacetic acid (EDTA) reduction solutions.

The following reducing agents were used in this study: disodium salt of EDTA (Chem-supply,  $\geq 97\%$  purity), tri-sodium citrate dihydrate (VWR,  $\geq 99\%$  purity), sodium borohydride (Scharlau,  $\geq 98\%$  purity), oxalic acid (BDH chemicals,  $\geq 99.5\%$  purity), L-ascorbic acid (Sigma-Aldrich,  $\geq 99\%$  purity), citric acid (Chem-supply,  $\geq 99\%$  purity), hydrazinium sulfate (Ajax Chemicals,  $\geq 98\%$  purity), hydroxylammonium sulfate (Ajax Chemicals,  $\geq 98\%$  purity), and triethylamine (Sigma-Aldrich,  $\geq 99\%$  purity).

### 2.2. PIM manufacturing

PIMs consisting of 70 wt% PVC, 20 wt% Aliquat 336 and 10 wt% 1-dodecanol or 70 wt% PVC and 30 wt% Aliquat 336 were prepared by a casting method reported in a previous study [10]. In this method the membrane components were dissolved in a small volume (e.g., 8–10 mL) of THF for the preparation of the PIM casting solutions. Each PIM casting solution was poured into a glass ring with a diameter of 7.5 cm which was positioned on a flat glass plate. The ring was covered with a watch glass to allow gradual evaporation of THF over 24 h. The PIMs fabricated by this method were optically transparent and homogenous as reported in previous studies (i.e., [10, 20] for PIMs containing both Aliquat 336 and 1-dodecanol and [21] for PIMs containing only Aliquat 336) and had an average thickness of  $30 \pm 5 \mu\text{m}$ . Circular sections of 2.5 cm in diameter and an average mass of 30 mg were cut from the PIMs and used in the experiments.

### 2.3. Au NP synthesis

Au NPs were synthesized by the procedure proposed by Bonggotgetsakul et al. [10] which involved extraction of Au(III) into a PIM for a predetermined period of time (loading time) while stirring the feed solution. The feed solution used for 2.5 cm diameter PIM circular sections was 50 mL and consisted of  $0.5 \text{ mol L}^{-1}$  HCl and Au(III), with a concentration of  $100 \text{ mg L}^{-1}$  in most experiments. This was followed by immersion of the 2.5 cm in diameter circular section loaded with Au(III) into a 50 mL of a mechanically stirred solution containing a suitable reductant (usually in concentration of  $0.1 \text{ mol L}^{-1}$ ) capable of reducing Au(III) to metallic Au for a predetermined period of time (reduction time). Table 1 lists all the loading and reduction conditions used in the present study. It should be noted that this table does not present the conditions for the individual experiments.

### 2.4. Instrumentation

All SEM images included in this work were obtained using an FEI Quanta 200 microscope. Secondary electron imaging mode under high vacuum with an Everhart-Thornley detector was used for all NP samples. Due to the presence of a surface coating of Au NPs, conductive sputter coating of samples prior to imaging was unnecessary, with the exception of images of fresh PIMs. Size estimation by SEM was done by manual measurement using ImageJ software with BioFormats plugin of

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