



# Poly-thiosemicarbazide/gold nanoparticles catalytic membrane: In-situ growth of well-dispersed, uniform and stable gold nanoparticles in a polymeric membrane



L.F. Villalobos<sup>a</sup>, P. Neelakanda<sup>a</sup>, M. Karunakaran<sup>a</sup>, D. Cha<sup>b</sup>, K.-V. Peinemann<sup>a,\*</sup>

<sup>a</sup> Advanced Membrane and Porous Materials Center, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia

<sup>b</sup> Advanced Nanofabrication, Imaging and Characterization Laboratory, King Abdullah University of Science and Technology (KAUST), 23955-6900 Thuwal, Saudi Arabia

## ARTICLE INFO

### Article history:

Received 5 August 2013

Received in revised form 19 October 2013

Accepted 22 October 2013

Available online 8 December 2013

### Keywords:

Gold nanoparticles

Polymeric membrane

Polythiosemicarbazide

In-situ growth

Catalytic membrane

## ABSTRACT

This work presents a method that achieves the highest loading, published so far, of non-agglomerated and well-distributed gold nanoparticles (AuNPs) inside a polymeric membrane. The method uses polythiosemicarbazide (PTSC) as the starting material for fabricating the membranes. This polymer contains one chelate site per monomeric unit, resulting in a high content of adsorption sites. This helps to achieve such high loading without agglomeration, along with the strong interaction of the chelate sites with the metal ions and the fact that they are distributed homogeneously along the membrane structure.

The simple and scalable three-step procedure developed in this work resulted in a PTSC membrane containing 33.5 wt.% Au/PTSC in the form of 2.9 nm AuNPs. The membrane demonstrated catalytic activity for the reduction of 4-Nitrophenol (4-NP) to 4-Aminophenol (4-AP).

© 2013 Elsevier B.V. All rights reserved.

## 1. Introduction

Polymeric membranes and metal nanoparticles (MNPs) have unique characteristics, however by putting them together some of this characteristics can be enhanced and tailored for a desired application. Some of the benefits obtained by this combination are (i) lower agglomeration and corrosion of the MNPs, (ii) controlled nanoparticle size due to steric effects and often different interactions between polymer and nanoparticles, (iii) tailored transport of molecules through the membrane and mechanical stability by embedding nanoparticles inside membrane matrix, (iv) modified electronic and optical responses due to the dielectric environment produced by the polymer around the nanoparticles. For this reasons scientists have investigated membrane-supported nanoparticles for applications such as catalysis, sensing, and facilitated transport.

Metal nanoparticles are at the frontier of heterogeneous and homogeneous catalysis [1], achieving remarkable selectivity and efficiency due to their high surface area, and easy recovery and recyclability (specially if they are attached to a support) [2]. The mild conditions where metal nanoparticles are able to perform catalysis [3] make polymeric membranes a promising support for them.

Gold nanoparticles are very stable and active nanoparticles; they are a topic of much current interest for their promising size dependent electronic, magnetic, optical, and catalytic properties [4,5]. To obtain AuNPs supported in a polymeric matrix two main routes can be followed: dispersion and physical immobilization of preformed nanoparticles in the polymeric matrix [6–9], and in-situ growth of the nanoparticles inside the matrix [10–13]. In general terms, the later avoids the necessity of preforming the nanoparticles, reduces its aggregation, and is easier to implement [14,15].

Several in situ methods have been proposed for the growth of metal nanoparticles inside a polymeric membrane. A common approach is mixing the metal precursor with the polymeric solution for future casting and reduction. This method gives good results at low metal precursor concentrations, but nanoparticles size increases at higher metal loads [10,15]. Another approach is the incorporation of an external agent able to trap metal ions to an already made polymeric membrane; some examples are the incorporation of a liquid anion exchanger in a plasticized polymeric membrane [11,13], layer-by-layer adsorption of polyelectrolytes on the surface of the membrane or inside the pores [16], and in situ polymerization of polyelectrolytes inside the membrane pores [17]. After incorporation of the external agent, the membrane is submerged in a solution containing the desired metal precursor, the membrane adsorbs metal ions, and finally a reduction step forms the nanoparticles. The limitation of this method is that the maximum loading of metal nanoparticles is controlled by the amount of

\* Corresponding author. Tel.: +966 2 8082769.

E-mail address: [klausviktor.peinemann@kaust.edu.sa](mailto:klausviktor.peinemann@kaust.edu.sa) (K.-V. Peinemann).

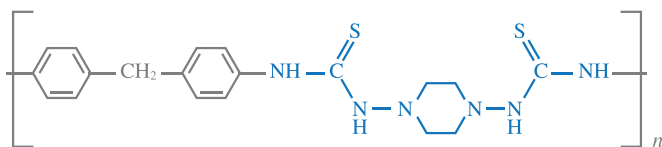


Fig. 1. Structure of poly-thiosemicarbazide.

external agent that we are able to incorporate in the membrane. Several adsorption-reduction steps can be done to increase the loading of metal nanoparticles but this will lead to agglomeration of nanoparticles and bigger sizes.

To simplify the fabrication process, achieve higher loadings and have more tune-ability of the membrane for different applications, we looked for a polymer that can form complexes with metal ions by itself, and that could be precipitated into membranes by a non-solvent induced phase separation process. The polymer we used is poly-thiosemicarbazide. This polymer contains a chelate site in each monomeric unit formed by two thiosemicarbazide units, as can be observed in the blue portion of Fig. 1. These chemical groups form very strong chelate complexes with several metal ions making this polymer a promising candidate for the application presented in this work. Campbell et al. demonstrated that this polymer forms chemical complexes with iron, nickel, silver, copper, mercury, and lead [18,19]. Further tests from our part confirmed that it also forms complexes with gold, palladium, and platinum, which are very attractive for catalytic applications. In the present work, we developed a method to fabricate PTSC asymmetric membranes and to grow gold nanoparticles inside the membrane matrix in a simple and scalable three step procedure.

## 2. Experimental

### 2.1. Materials

Dimethyl sulfoxide (DMSO), 1,4-dioxane, 4-nitrophenol (4-NP), hydrochloric acid (HCl) (all from Sigma–Aldrich Co.), and sodium borohydride ( $\text{NaBH}_4$ ) (from Fisher Scientific Co.), were used as received. The gold solution used in this work is produced by PerkinElmer Co. and is labeled gold (Au) Pure AS Calibration Standard 1000 ppm in 10% HCL. At room temperature and at the pH of this solution, Au(III) is more stable than Au(I) and the predominant species is the square planar  $\text{AuCl}_4^-$  complex [20]. Poly-thiosemicarbazide was synthesized according to literature

by the reaction of N,N'-diaminopiperazine and methylenebis(4-phenylisothiocyanate) in DMSO [19].

### 2.2. Membrane preparation

The membrane was prepared by non-solvent induced phase separation. The membrane casting solutions contained 15 wt.% PTSC, 10 wt.% 1,4-dioxane and 75 wt.% DMSO. The preparation process consisted on casting a 250  $\mu\text{m}$  thick film on a glass plate with a doctor blade, followed by immersing the glass plate in a non-solvent bath (water) at room temperature for at least 12 h. After casting the membranes were stored in a water/ethanol solution until use. The time of storage ranged from one day up to two months.

### 2.3. In-situ growth of AuNPs

#### 2.3.1. Gold adsorption experiments

PTSC membrane squares of 1  $\text{cm}^2$  were submerged in 10 ml gold solutions containing different initial concentrations: 1000, 500, 100 ppm. The gold solutions were prepared by diluting the gold (Au) Pure AS Calibration Standard 1000 ppm with appropriate amounts of 10% HCl solution. The gold concentration in the solutions was monitored through out 24 h by taking 0.2 ml samples and analysing them by using inductively coupled plasma optical emission spectrometry (ICP-OES) (Varian 720-ES).

#### 2.3.2. Optimized process to fabricate PTSC/AuNPs membranes

PTSC membranes were cut in circles with 2.5 cm of diameter and an average dry weight of 14.3 mg. The nanoparticle growth process (Fig. 2) consisted of the following steps: (i) immersion of the membrane sample in 22 ml of gold (Au) Pure AS Calibration Standard 1000 ppm in 10% HCl solution for 10 min, (ii) thorough washing for five minutes with water and store it in water for one hour, (iii) immersion in a 0.05 M  $\text{NaBH}_4$  bath of 15 ml for two minutes, (iv) transfer it to a water/ethanol solution and keep it there until use.

### 2.4. Membrane and AuNPs characterization

A Millipore stirred cell of 10 ml was used to measure the flux before and after the growth of the nanoparticles. Each membrane was tested at least 10 times in order to get a trustworthy result.

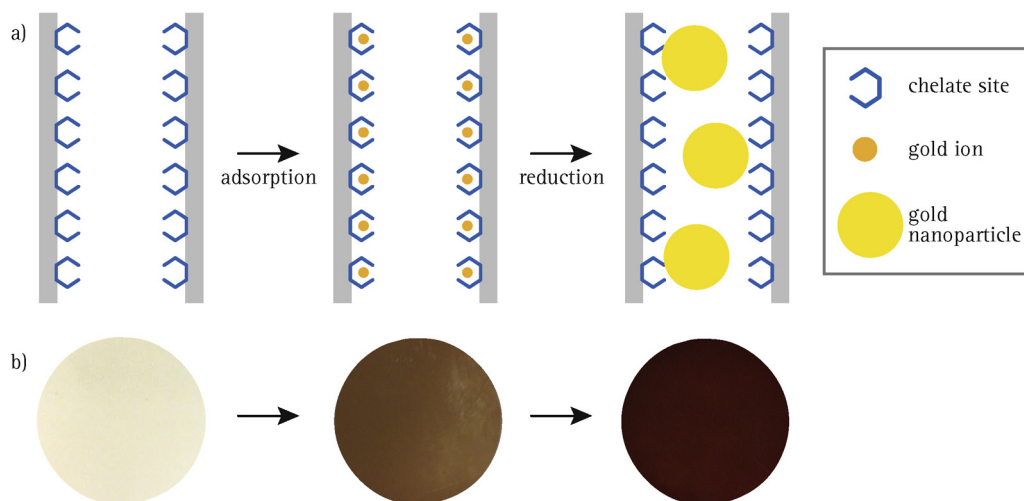


Fig. 2. Growth of gold nanoparticles in the PTSC membrane. (a) Schematic diagram showing the gold ions adsorption and Au nanoparticles formation in the membrane. (b) Real-life pictures of the membrane going through this process.

Download English Version:

<https://daneshyari.com/en/article/54073>

Download Persian Version:

<https://daneshyari.com/article/54073>

[Daneshyari.com](https://daneshyari.com)