



Controlling formation of gold nanoparticles generated *in situ* at a polymeric surface



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ABSTRACT

This work shows that *in situ* reduction of metal ions bound at a polymer surface can form nanoparticles within the polymer matrix as well as at the interface, and the size and distribution of nanoparticles between the interface and subsurface depends upon the choice of reagents and reaction conditions. Tetrachloroaurate ions were bound to cross-linked SU-8 films that were functionalized using a variety of multi-functional amines, then reduced using one of several reagents. Reduction using sodium borohydride or sodium citrate generates bands of interspersed gold nanoparticles as much as 40 nm deep within the polymer, indicating that both the Au ions and the reducing agent can penetrate the surface enabling formation of nanoparticles within the polymer matrix. Nanoparticle formation can be confined nearer to the polymer interface by reducing with hydroquinone, or by processing the polymer film in aqueous media using high molecular-weight multifunctional amines that confine the gold ions at the interface.

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1. Introduction

Gold nanoparticles (Au NPs) and clusters or arrays of surface-bound Au NPs have a wide variety of applications, including nanofabrication, optical devices, and catalysis [1–11]. Au NPs and nanoparticle-aggregates are effective for enhancing signal via surface plasmon resonance in various spectroscopic and sensing methods [12,13]. Metal nanoparticles (NPs) are used as nucleation sites in electroless metallization, which is a promising approach for creating metallized micro-electromechanical structures (MEMS) and optical MEMS devices [7,14–18]. Such applications frequently involve Au–NP functionalization of a polymeric surface or structure. As such, NP synthesis and surface functionalization continue to be active areas of research that impact many established and emerging technologies.

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The common approach for functionalizing surfaces with NPs involves first synthesizing colloidal particles in solution and subsequently binding them to the surface of interest, using the Turkevich method [7,8,12,18–21] or sodium borohydride (NaBH₄) reduction [13,20,22–25]. In contrast, *in-situ* reduction of gold ions adsorbed onto a surface is an alternative means for generating Au NP-functionalized surfaces and devices [1,2,26–30]. This approach offers some advantages, including the possibility for generating smaller particles, stabilization of the NPs through surface attachment, and decreased aggregation due to immobilization on the surface [1,30,31]. Additionally, surface-bound NPs can be readily isolated from the synthesis medium or further derivitized by simple physical transfer of the supporting substrate. There are several pioneering reports of *in-situ* synthesis of Au NPs at polymeric surfaces [1–3,28,30–33]. Yet in comparison to the conventional approach of separately synthesizing NPs then binding them to a surface, *in-situ* synthesis of Au NPs at polymeric surface remains far less explored. In this work we show how the choice of gold-ion surface-linker and reducing agent affects *in-situ* formation of Au NPs at the surface of a polymer known as “SU-8”. SU-8 is a cross-linkable epoxide which is increasingly employed for patterning micro- and nano-scale surfaces and creating functional devices [25,34–36]. The key findings of this work are (1) NPs formed by *in-situ* reduction do

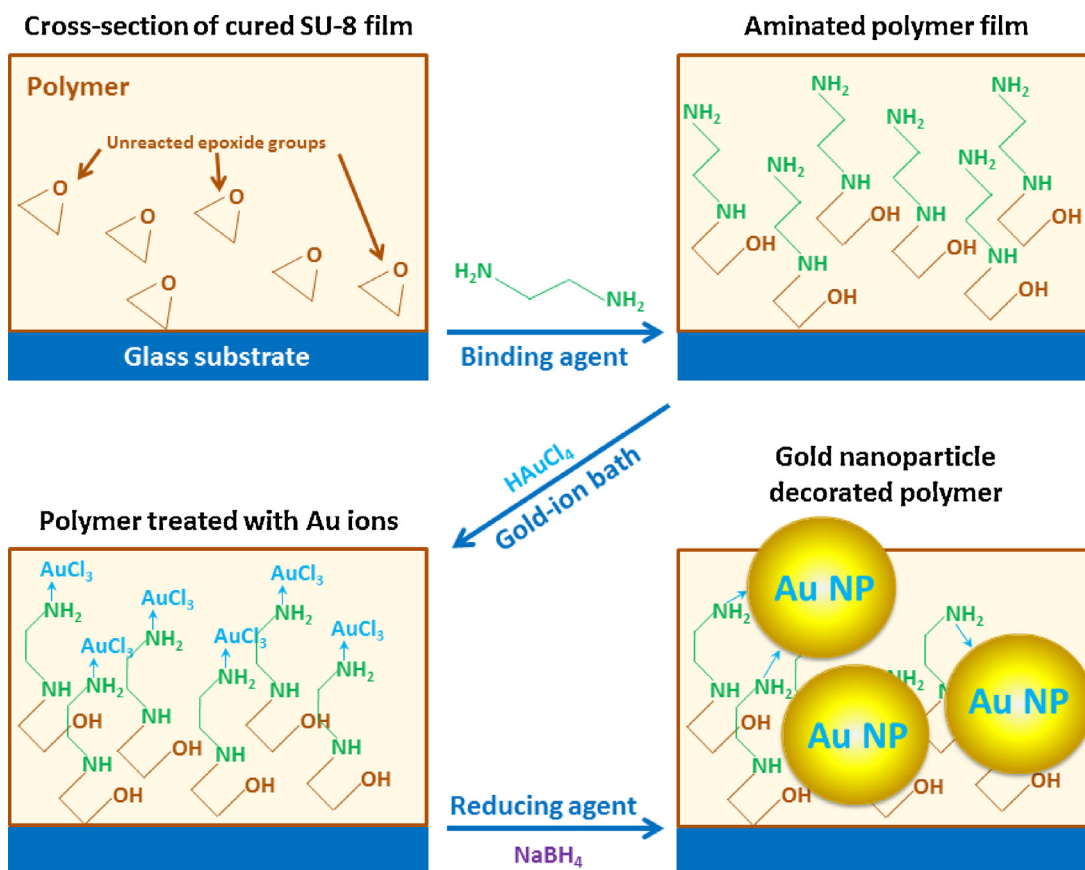


Fig. 1. Illustration of the process used to functionalize the surface of cross-linked polymer SU-8 with Au NPs. Each panel represents a cross-section of the polymer film through the surface. The scheme is illustrated for the case in which Au ions are bound to the polymer film surface using ED then reduced by NaBH_4 , and only one possible mode of Au-amine interaction is represented.

not reside exclusively at the liquid-polymer interface; (2) varying the reducing agent can affect both the size of the NPs and their location relative to the interface; and (3) formation of Au NPs can be confined to the liquid-polymer interface by judicious choice of the amine binding agent and how it is processed.

2. Material and methods

2.1. Preparation of gold nanoparticle functionalized films

All commercial materials were reagent grade and used as received unless otherwise indicated. Deionized water (18 M Ω) was used to rinse all samples and prepare all aqueous solutions. The process of polymer surface modification is illustrated in Fig. 1, for the case of the binding agent ethylenediamine (ED) and reducing agent NaBH_4 . All reactions and solution preparation were carried out under ambient conditions unless otherwise stated.

Square glass coverslips (25 mm, no. 1 thickness) served as substrates and were cleaned by immersion in an aqueous 1 M KOH bath (Aldrich and Fisher, technical grade) for 1 h followed by drying in an oven at 100 °C for 20 min. Cross-linked SU-8 films were prepared by spin coating the epoxide resin (SU-8 2035, Microchem) onto cleaned substrates. Solvent was removed from the resin film by baking the samples on a hotplate. The samples were placed on a hotplate at room temperature, heated over a period of one minute to 95 °C, held at this temperature for 9 min, then the hot plate was switched off and the samples were allowed to cool to room temperature (*circa* 10 min). The resin films were subsequently irradiated for 2 min through a long-pass filter (Omega Optical, PL-360LP, 360-nm cut off) with a broad-band UV lamp (Loctite

ZETA 7411-5, 400 W metal halide source, 315–400 nm) then baked to activate cross-linking using the same conditions as the pre-exposure bake.

Cross-linked polymer surfaces were activated toward binding Au cations by covalently attaching one of several multifunctional primary amines (Fig. 2). Functionalization with ED was achieved by immersing the cross-linked polymer film into a 20% (v/v) of ED (Alfa Aesar, CAS no. 107-15-3) in ethanol for 1 h [37,38]. Functionalization with tetraethylenepentamine (TEPA, CAS no. 112-57-2) and *N*-aminoethylpiperazine (AEP, CAS no. 140-31-8) were similarly achieved by immersing samples in 20% (v/v) aqueous solutions of the amines for 1 h. Following amination, all samples were rinsed with copious water and allowed to dry by standing in air.

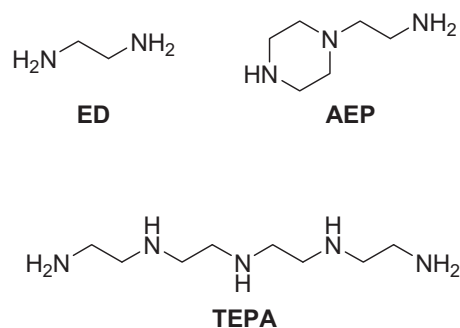


Fig. 2. Multi-functional amines used to bind gold cations to the surface of cross-linked SU-8.

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