

# A Facile Method for Micropatterning of Gold Nanoparticles Immobilized on UV Cross-linked Polymer Thin Films

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This report demonstrates the immobilization of uniformly sized gold nanoparticles (AuNPs) on UV cross-linked poly(4-vinylpyridine) (P4VP) polymer thin films and the preparation of micropatterned structures of AuNPs on these films. The polymer thin films were prepared by a spin-coating of P4VP onto a cleaned silicon wafer surface. Upon UV irradiation, these films were then photo cross-linked. Gold nanoparticles were immobilized by immersing the polymer surface in a colloidal solution of gold nanoparticles stabilized by citric acid. The morphology of the films and the immobilization of AuNPs were studied by atomic force microscopy (AFM) and UV-visible spectroscopic techniques. The micropatterned gold structures that were produced on the polymer surface are delineated by combining with the photolithographic method. While untreated and simply spin coated films were physisorbed and unstable that could be easily removed by rinsing with a solvent, the cross-linked and AuNPs immobilized P4VP films were found to be highly stable even after repeated solvent extractions.

**Keywords:** Gold nanoparticles, Immobilization, Lithographic pattern, Poly(4-vinylpyridine), UV irradiation

## 1. INTRODUCTION

Metal nanoparticles have attracted immense interest due to the high and specific impacts in the fields of biotechnology and bioscience[1-4]. Being a noble metal, gold is widely investigated due to the unusual properties different from those of bulk states and potential applications in optics, electronics, magnetics, catalysts, and chemical and biochemical sensing technologies[5-9]. A variety of polymer molecules have been selected to decorate the surface of gold and silver nanoparticles (AuNPs) for a number of purposes[10-13].

Polymer thin films (which can be fabricated onto solid substrates either by covalent or non-covalent approaches) play a vital role for creating responsive surfaces[14-16]. While solution casting and spin coating are the commonly used techniques, the films produced are physisorbed and can be easily removed by rinsing with a solvent. Such processes could be chaotic as this could be detrimental to the final structure and the nano-patterns emerging. On the other hand, covalently immobilized films are more robust towards environmental processing and are firmly attached to the substrate. However, the synthetic chemistry behind these techniques involves multistage processing which are complicated and challenging. One of the versatile methodologies for the production of polymer thin films on substrates is a simple UV induced irradiation technique, which has proven highly efficient[17]. The advantage is that the method is extremely simple as the process only involves spin coating the polymer on a substrate followed by UV irradiation. This polymer thin film can withstand extensive solvent extraction at elevated temperatures and makes this approach attractive[18].

Among the various polymers, poly(4-vinylpyridine) (P4VP) has been widely used as a universal surface modifier

because of the ability to undergo hydrogen bonding with polar species and the strong affinity of the pyridyl group towards metals[19]. In addition, P4VP is an interesting material because of the electrostatic interactions with anions in the quaternized or protonated form in addition to the high ability to form charge transfer complexes with acidic dopants[20]. The surface modified thin films containing the quaternized P4VP derivatives are known to possess antibacterial activity[21]. Interestingly, the polycations of P4VP were also reported to be useful in biomedical applications as efficient non-viral gene delivery vectors[22,23]. P4VP (being a UV sensitive polymer) can be easily patterned in a micrometer scale by selective UV exposure.

Inspired by such properties of P4VP and the importance of AuNPs, this study is the first to report the efficient immobilization of AuNPs on UV cross-linked P4VP polymer thin films. Furthermore, micropatterned polymer surfaces were created by a photolithography technique and were used for the immobilization of AuNPs. This method enjoys at least two advantages. (1) The high efficiency and simplicity to immobilize nanoparticles by UV induced lithography. (2) The stability of the immobilized AuNPs was exceptionally high on P4VP surfaces due to cross-linking and the method does not involve chemical derivatization of either the substrate or the polymer, and yet adheres to the substrate that could withstand extensive solvent extraction.

## 2. EXPERIMENTAL

**Materials:** Poly(4-vinylpyridine) (Mw = 160,000 g/mol), hydrogen tetrachloroaurate (III) (gold solution (30 wt.% in HCl)) and other chemicals were purchased from Aldrich. All other reagents were analytical grade (Junsei, Japan) and used as received.

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## Methods:

### 2.1 Preparation of polymer thin films on silicon surfaces

Silicon wafers were cleaned in a piranha solution (7:3 v/v 98 % sulfuric acid/35 % hydrogen peroxide) with stirring at 90 °C, washed thoroughly with deionized water and dried under a gentle stream of nitrogen prior to polymer coating. A 10 mg/mL solution of P4VP in 2-butanol was spin coated using a spin coater E.H.C. model SC-300 onto the cleaned wafer surface at 2000 rpm for about a minute. The polymer coated thin films were further UV irradiated with a 10 watt low pressure Hg lamp for 1 min. The unbound polymers were removed by soaking with 2-butanol.

### 2.2 Preparation and immobilization of AuNPs onto P4VP thin films

All glassware used in the following procedure were cleaned in a bath of freshly prepared solution of (3:1) HNO<sub>3</sub>-HCl, washed thoroughly with water and dried prior to use. The ~20-nm-diam Au colloid was prepared, with a slight modification as reported elsewhere[24]. A solution of Au colloid particles were prepared by mixing 0.275 mL of 1 % trisodium citrate and 0.750 mL of 0.075 % NaBH<sub>4</sub> / 1 % trisodium citrate with 100 mL of distilled H<sub>2</sub>O / 0.500 mL 1 % HAuCl<sub>4</sub> solution, and stirring 5 hours at a constant speed. The color change observed indicated the formation of AuNPs. The immobilization of AuNPs onto the spin coated, UV cross-linked P4VP thin films were carried out by simply immersing them in the Au colloid for different time intervals. The films were then removed, washed with distilled water, and dried in a stream of nitrogen.

### 2.3 Micropatterning of AuNPs on P4VP thin films

Patterning of P4VP was performed in the following method. Followed by spin coating of the polymer, the resulting thin film was covered with a quartz crystal photomask (5x5 cm in area with an exposed area of 2x2 cm). UV light was passed in order to crosslink the exposed area and the mask was removed by soaking it in the 2-butanol. The obtained patterned films were used for the immobilization of AuNPs as described above. Morphological results were obtained on a field emission scanning electron microscopy and force microscopic studies.

### 2.4 Characterization techniques

The polymer film thickness was measured on a Gaertner model L2W16E ellipsometer with a He/Ne laser at an incident angle of 70 °C. The refractive indices used to calculate the film thickness was 1.581 for P4VP. The absorption spectra of the thin films on quartz substrates were obtained using an ultraviolet-visible spectrometer (Perkin Elmer Lambda 40) while the surface morphology of the polymer thin films and immobilized AuNPs on the films were studied by atomic force microscopy AFM (Digital Instruments (USA), multimode TM SPM).

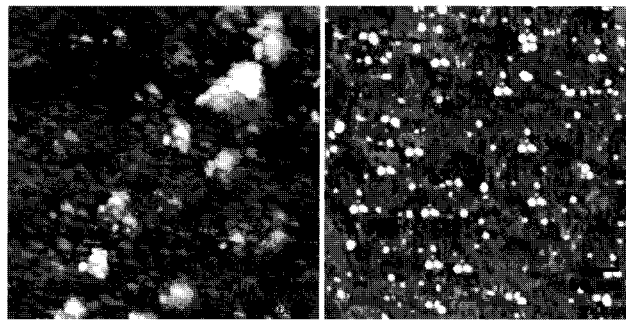


Fig. 1. AFM micrographs of AuNPs immobilized onto P4VP thin films by (A) non- cross-linking and (B) cross-linking method.

## 3. RESULTS AND DISCUSSION

An advantage of using polymers as the surface modifier is that polymer chains can entangle to form an interpenetrated network. There are several polymers that undergo a direct attachment of polymer films onto solid substrates by UV irradiation, for instance, polystyrene, polyvinyl chloride, and P4VP[17]. This study spin coated the P4VP thin films followed by a UV cross-linking technique. The irradiation was carried out in air with a 10 watt low pressure Hg lamp for about a minute. The immobilization of P4VP was achieved and was the result of photochemically induced cross-linking of the polymer to the substrate surface. The obtained samples were extracted with a suitable solvent (2-butanol or methanol) to remove the unbound polymer. The thicknesses of the resulting films were measured using ellipsometry at different irradiation times. A thickness of 43nm was obtained for P4VP thin films after UV irradiation and solvent extraction. P4VP films attained maximum thickness at a shorter exposure time (1 min) and the thickness remained constant after a longer exposure period. The UV cross-linked polymer thin films were then immersed in an Au colloid solution for a desired time in order to immobilize the AuNPs.

Figure 1 shows the AFM topography of the AuNPs immobilized P4VP films. After solvent extraction, discrete AuNPs were uniformly distributed on the films prepared by a UV cross-linked method(see Fig. 1(B)), whereas highly aggregated particles were obtained in non cross-linked polymer films(Fig. 1(A)). This aggregation could be due to the detachment of the polymer chain from the film surface during the immersion of the film in a colloidal solution, facilitating the aggregation of nanoparticles. Noted is that while untreated and simply spin coated films were physisorbed, unstable, and could be easily removed by rinsing with solvent, the UV cross-linked followed by AuNPs immobilized films were found to be highly stable even after repeated solvent extractions. AFM micrographs confirmed that the morphology of AuNPs was retained by cross -linked films.

It is acknowledged that the adsorption of metal ions and metal nanoparticles from aqueous solution to a substrate surface is usually controlled by the properties of the surface. In particular, surface functional groups such as amino, carboxyl, thiol, and pyridyl can be used to facilitate the adsorption of metals ions and metal nanoparticles[25]. The

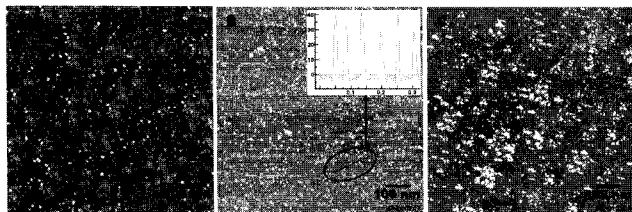


Fig. 2. AFM micrographs of AuNPs immobilized at different immersion time. (A) 5 min, (B) 15 min, and (C) 30 min. Inset figure (B) corresponds to the vertical distance profile.

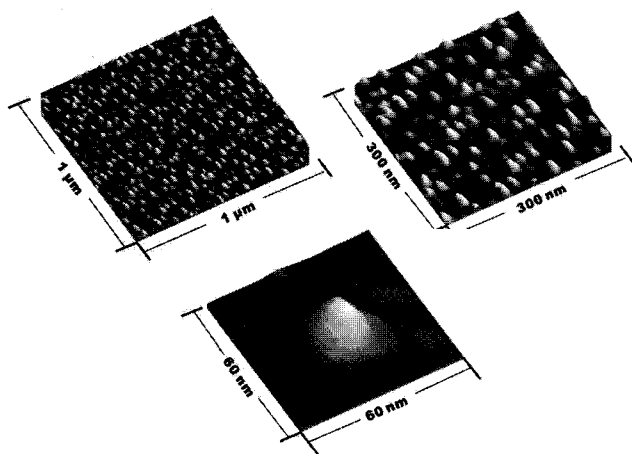


Fig. 3. 3-D AFM images of AuNPs immobilized for 15 min. Figures at different magnitude are shown.

effective immobilization of AuNPs on the cross-linked P4VP surfaces can be attributed to the strong affinity of the pyridyl groups to metals through the polar interaction or electrostatic interaction between negative citrate ion protected gold nanoparticles and positively charged pyridyl groups[19,25].

The P4VP films were immersed in the Au colloidal solution for different time periods in order to optimize the immobilization conditions since different amounts of gold particles could be deposited on the polymer thin film depending on the time of immersion. Figure 2 shows the AFM images of films immobilized at 5, 15, and 30 min. The results suggest that 15 min of immobilization is optimal. At longer immersion periods, AuNPs tend to severely aggregate on the cross-linked polymer films. 3-D AFM images taken on 15 min immobilized film,(Fig. 3) confirmed that the particles have an average diameter of around 20 nm and are almost evenly distributed.

The UV-visible absorption spectra of the P4VP film and AuNPs immobilized P4VP films on quartz substrate were recorded to confirm the presence of AuNPs on the cross-linked polymer films(Fig. 4). An absorption band at 540 nm is observed, which is attributed to the surface plasmon resonance of AuNPs present on the polymer films. The results are consistent with literature reports[26]. The spike at 375 nm is obtained due to lamp change during the UV recordings.

Since the immobilization of P4VP film was an UV induced process, a lithography technique was employed to

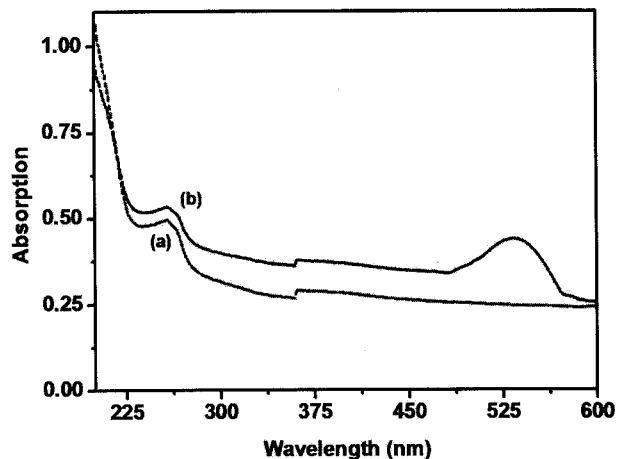
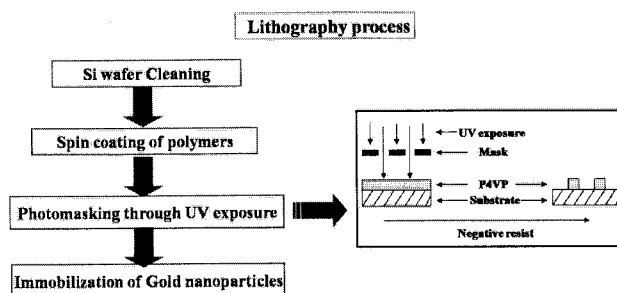


Fig. 4. UV absorption spectra of (a) bulk P4VP and (b) AuNPs immobilized on cross-linked P4VP film.



Scheme 1. Lithography process for patterning P4VP thin films.

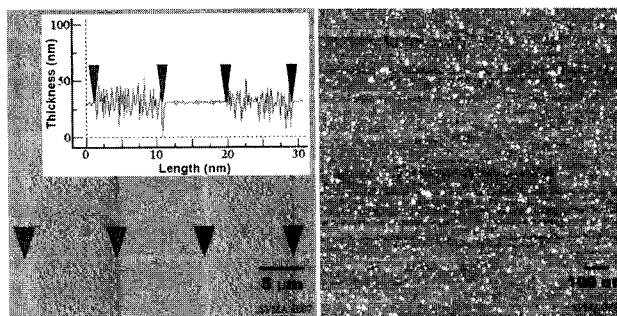


Fig. 5. Patterned AFM and AuNPs immobilized P4VP films. Inset figure shows the vertical distance profile of the exposed and unexposed area.

pattern the polymer thin films(Scheme 1). In general, (depending on the time of immersion) different amounts of gold can be deposited on the illuminated areas, while no immobilization of AuNP was observed in the non-illuminated areas. An AFM image taken on the 15 minute immobilized sample demonstrates the formation of the micropatterned gold structures on the films(Fig. 5). The patterning of the AuNPs immobilized P4VP polymer thin film was further studied and the thickness difference between the exposed and unexposed areas were investigated. The vertical distance of the pattern was found to be around 43 nm, which was in good agreement with the obtained ellipsometry results. Furthermore, the reproducibility of this method (including the ability to pattern over

topography) clearly depict that the gold nanoparticles can be easily immobilized in spatially defined polymer thin films by photolithography and micro-scale structures of gold in different amounts could be derived with considerable ease.

#### 4. CONCLUSION

In this approach, the efficient immobilization of Au nanoparticles onto the UV cross-linked P4VP thin films is presented. The films were conveniently prepared by spin coating followed by irradiation. The morphology images derived from AFM studies confirmed the uniform immobilization of AuNPs on the cross-linked P4VP film, which was further supported by a UV absorption band obtained at 540 nm. While non-cross-linked films were physisorbed and easily removed by rinsing with solvents, the cross-linked and gold immobilized films were found to be stable even after repeated solvent extractions. The effective immobilization of AuNPs on the polymer films can be attributed to the strong affinity of the pyridyl groups to metals through the polar covalent interaction. The technological implication of this approach is that spatially defined polymer thin films could be fabricated with uniformly distributed metal nanoparticles by a simple lithography process.

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