

Selective Immobilization of Gold Nanoparticles on the Surface of a Photoreactive Polymer

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Summary. A photoreactive polymer containing thiocyanate (SCN) groups was employed for the immobilization of gold nanoparticles (AuNP). Upon UV illumination, isothiocyanate (NCS) groups are generated at the surface by photoisomerization. The illuminated areas of the polymer layer containing NCS were selectively modified with 2-aminoethanethiol to give SH terminated thiourea units at the surface. Gold nanoparticles were selectively immobilized in these areas by immersing the polymer surface in a colloidal solution of gold nanoparticles stabilized by citric acid. Depending on the time of immersion, different amounts of gold were deposited on the illuminated areas, while no immobilization of AuNP was observed in the non-illuminated areas. By using photolithographic masks, patterned gold structures (μm scale) were produced on the polymer surface.

Keywords. Polymer; Photochemistry; Surface; Gold; Nanoparticle.

Introduction

Gold is the material of choice in many electronic applications, especially in telecommunication, information technology, and other high performance applications. Gold has outstanding resistance to corrosion, it is easy to work with, and has a high thermal and electrical conductivity. Through the use of nanotechnology many other applications have become accessible, which are related to the unique properties of nanoparticles. Gold nanoparticles (AuNP) are cur-

rently used in various applications such as sensor elements [1, 2, 3], optical devices [4], optical coding systems, and high quality security features [5, 6]. In many cases patterned gold layers at surfaces and interfaces are required. To obtain such structures by deposition of AuNP, several strategies can be followed. It is possible to carry out the deposition of AuNP on prefabricated structures made with photoresists [7] and to apply polydimethylsiloxane (PDMS) stamps for microcontact printing of thiols, which act as anchoring groups for AuNP [8]. In another approach, AuNP can be manipulated by AFM tips [4] and deposited in selected surface areas. These approaches have in common that they are time-consuming or involve several steps to achieve the desired patterns. In this contribution we present a straight-forward approach which relies on UV sensitive surfaces.

We employed the photoreactive copolymer poly(styrene-co-4-vinylbenzyl thiocyanate) (*PS-co-VBT*) [9]. Upon UV illumination with $\lambda < 300$ nm, the thiocyanate (SCN) groups undergo a free radical isomerization to isothiocyanate (NCS) groups. In previous contributions we have reported that the photogenerated NCS groups in films of *PS-co-VBT* can react with gaseous amines to give thiourea units [10] while the non-illuminated areas (containing only SCN groups) are inactive towards amines at 20°C. All these reactions can be followed quantitatively by infrared spectroscopy.

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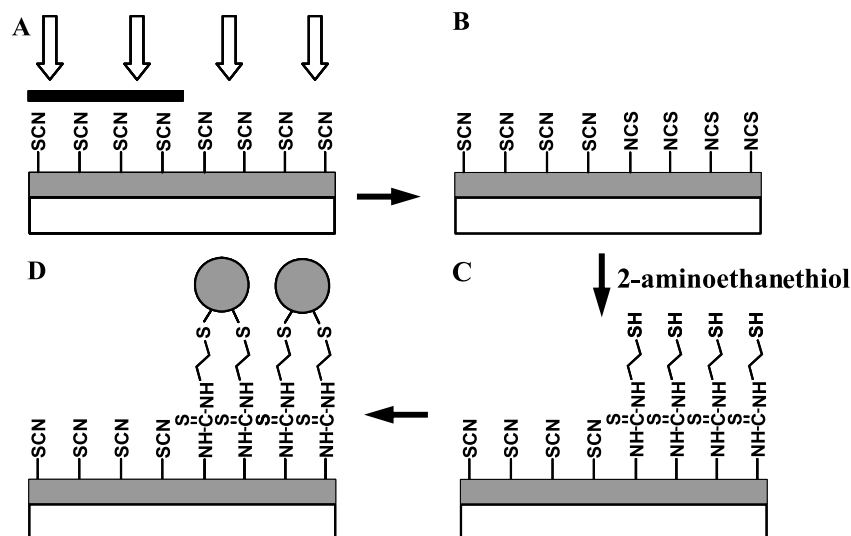


Fig. 1. Reaction scheme for immobilizing AuNP at the polymer surface. (A) *PS-co-VBT* spin coated on a Si wafer and exposed to UV light through a mask, (B) photoisomerization of SCN to NCS, (C) selective reaction of NCS with 2-aminoethanethiol, and (D) immobilization of AuNP from solution

Photochemical patterning of *PS-co-VBT* and other copolymers of the monomer VBT has been employed to create index and relief gratings, which can be used as diffractive elements in optically pumped DFB lasers [11]. Moreover, amino-terminated biomolecules can be immobilized at UV-irradiated surfaces of *PS-co-VBT* (biochip applications). Figure 1 displays the general photoreaction in *PS-co-VBT* and the post-exposure modification of NCS units with amines. In this study, the reaction was carried out with 2-aminoethanethiol. As a result, a surface bearing mercapto groups linked by thiourea units was obtained. Such modified surfaces are of interest for the immobilization of AuNP.

The synthesis of AuNP by reduction of gold(III) ions with citrate in water has been introduced by *Turkevitch et al.* in 1951 [12] and is well known nowadays. It is one of the most popular methods for generating AuNP and leads to particle diameters in the range from a few to approx. 150 nm. The diameter of AuNP can be varied by using different ratios between reducing and stabilizing agents [13] and by selected additives. For this work, we chose the *Turkevitch* method because AuNP bearing a shell of rather loosely bound citrate ligands on the gold core are obtained. The citrate shell can easily be replaced by thiol molecules, which provides a convenient route for immobilization techniques.

Results and Discussion

Photoreaction and Post-Exposure Modification of PS-co-VBT

The polymer *PS-co-VBT* was dissolved in anisole and spin-coated on CaF₂ discs. The cast films were dried, placed in an irradiation chamber, and then illuminated with a Hg lamp under nitrogen. Inert gas conditions prevented an unwanted photooxidation of the polymer film, which would lead to the formation of hydroxylic and carboxylic groups. Such groups can interfere in all following surface reactions.

To have a comparison of the reactions at the irradiated and non-irradiated zones of the polymer surface, an area of the sample surface was covered with a contact mask during illumination. All illuminations were carried out such that a maximum conversion of the SCN units to NCS groups was achieved. Immediately after illumination the samples were immersed in an aqueous solution of 2-aminoethanethiol. The kinetics of the addition of amines to isothiocyanates is strongly *pH* dependent since the concentration of the free base of aliphatic amines depends on the *pH*. For optimum post-exposure modification of the polymer surface with 2-aminoethanethiol the *pH* of the reaction solution had to be adjusted to 8.5–9.5. Under these conditions the addition of 2-aminoethanethiol to isothiocyanates yields almost exclusively the thiourea derivative [14]. The

addition of SH units to the NCS groups (which would give dithiocarbamates) is not observed. In all cases, the aqueous solution of 2-aminoethanethiol was prepared freshly before use to avoid degradation by oxidation reactions. By carrying out the reaction in aqueous medium the swelling of the polymer film during the reaction is negligible. Consequently, the polymer surface remains smooth and the modification proceeds only at the surface. With the reaction sequence in Fig. 1 the functional groups at the polymer surface were first transformed from SCN to NCS and then to free SH groups, which serve as anchoring units for the AuNP [15].

Immobilization of Gold Nanoparticles on the Polymer Surface

In the following experiments we employed an aqueous solution of citrate stabilized gold nanoparticles with an average diameter of 22 nm. This diameter was derived from optical spectra of the AuNP solution (diluted 1:3) which displayed a maximum of absorbance at $\lambda = 521$ nm. More detailed information on optical spectra of AuNP is available from literature (*cf.* Ref. [16]).

Immediately after photochemical modification, the samples were immersed in the AuNP solution for a well-defined time, rinsed with deionized water, and then dried. The amount of AuNP deposited at the polymer surface was assessed by recording UV-

VIS spectra. The following surfaces were compared with respect to their reactivity towards AuNP: (1) non-irradiated films of *PS-co-VBT* (exposed to 2-aminoethanethiol), (2) UV-irradiated *PS-co-VBT* (not exposed to 2-aminoethanethiol), and (3) UV-irradiated *PS-co-VBT* (exposed to 2-aminoethanethiol).

Figure 2 displays UV-VIS spectra of different polymer samples immersed in the AuNP solution for 5 min at 20°C. It can be seen that on non-irradiated films of *PS-co-VBT* no significant amounts of AuNP are deposited, regardless whether these surfaces had been exposed to the modifying agent 2-aminoethanethiol or not. In a similar fashion, surfaces of UV-irradiated *PS-co-VBT* (lacking the derivatization with 2-aminoethanethiol) are not capable of immobilizing significant amounts of AuNP. In both cases no absorbance in the spectral range 500–600 nm is discernible. In contrast to this, for samples of UV-illuminated *PS-co-VBT* films that had been modified with 2-aminoethanethiol an absorbance signal at $\lambda_{\max} = 539$ nm is well detectable after contact with the AuNP solution. For comparison, optical spectra of the AuNP solution (diluted 1:3) displayed a maximum of absorbance at $\lambda = 521$ nm which is attributed to surface plasmon resonance of isolated AuNP.

The above results demonstrate that gold nanoparticles are selectively immobilized at surface areas bearing SH groups. It is interesting to see that only small amounts of Au are deposited at UV-irradiated surface areas bearing NCS units, although isothio-

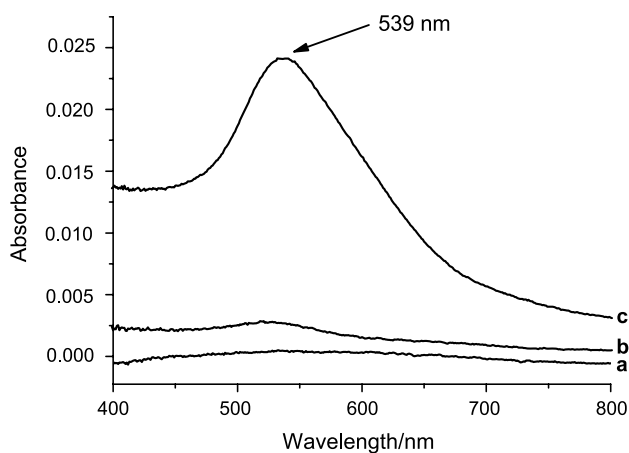


Fig. 2. Optical absorption spectra of polymer films after 5 min of immersion in the AuNP solution. (a) Non-irradiated *PS-co-VBT*, (b) irradiated *PS-co-VBT*, and (c) *PS-co-VBT* irradiated and subsequently modified with 2-aminoethanethiol

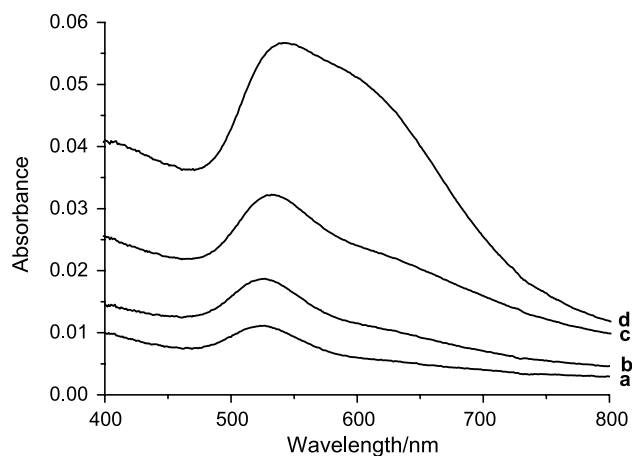


Fig. 3. Optical spectra of *PS-co-VBT* films (illuminated and modified with 2-aminoethanethiol) after different periods of immersion times in the AuNP solution (peak wavelength in nm). (a) 2 min (523), (b) 5 min (527), (c) 10 min (532), and (d) 20 min (541 and 603)

cyanates (e.g. benzyl isothiocyanate) have been reported to bind to AuNP capped with citric acid [17, 18].

Figure 3 contains optical absorption spectra of *PS-co-VBT* (UV-irradiated and subsequently modified with 2-aminoethanethiol) for different periods of immersion times in a diluted AuNP solution. With increasing time of immersion the amount of AuNP immobilized at the surface increases as indicated by gaining in UV-VIS absorbance in the spectral range 520–550 nm. At the same time, the peak maximum shifts to higher wavelengths. While after 2 min of immersion the peak is located at $\lambda_{\max} = 523$ nm (AuNP in diluted solution: $\lambda_{\max} = 521$ nm), the peak

position shifts to $\lambda_{\max} = 527$ nm after 5 min and to $\lambda_{\max} = 541$ nm after 20 min of immersion. After prolonged immersion times (10 and 20 min) an additional absorption signal (shoulder at $\lambda \sim 600$ nm) becomes discernible in the UV-VIS spectrum, see Fig. 3. The absorbance maxima in the range 520–550 nm can be attributed to single AuNP, clusters of AuNP, and islands of monolayers of AuNP and thus reflect the formation of a self-assembly of a two-dimensional array of closely packed Au nanoparticles [19]. The double-peaked spectrum observed after 20 min of immersion contains signals at 541 and ~ 600 nm. The long-wavelength peak has been attributed to plasmon–plasmon interactions between neighbouring AuNP [20] and is caused by a higher aggregation of AuNP at the surface. For a more detailed discussion of these phenomena, cf. Refs. [19, 20].

To confirm the results from optical spectroscopy, the deposition of AuNP at the polymer surface was investigated by AFM. Figure 4 shows AFM micrographs taken of the illuminated and subsequently SH modified polymer surface after immersion in the AuNP solution for 30 min (B) and for 60 min (C). For comparison, a surface of non-illuminated *PS-co-VBT* was immersed in the AuNP solution for 60 min and also investigated by AFM, see micrograph (A) in Fig. 4. While at the non-illuminated surface of *PS-co-VBT* only a few isolated nano-particles are detectable by AFM, the modified surface is covered with AuNP after 30 min and bears a densely packed surface layer of gold nanoparticles after 60 min. These AFM data are in agreement with the optical measurements.

Surface Patterning with Contact Masks

We further investigated if gold patterns can be created on the surface of our polymer. Honeycomb type copper grids (600 mesh), which are commonly employed for TEM measurements, were used as contact mask [21]. The polymer *PS-co-VBT* was cast on a CaF_2 disk, and after application of the copper mask the surface was illuminated. All further steps were carried out as described above with immersion in the AuNP solution for 60 min. Figure 5 shows the optical micrograph of the patterned gold layer. The patterned areas bearing a gold layer appear brighter than areas lacking the gold layer, because the micrographs were taken in the impinging light mode and

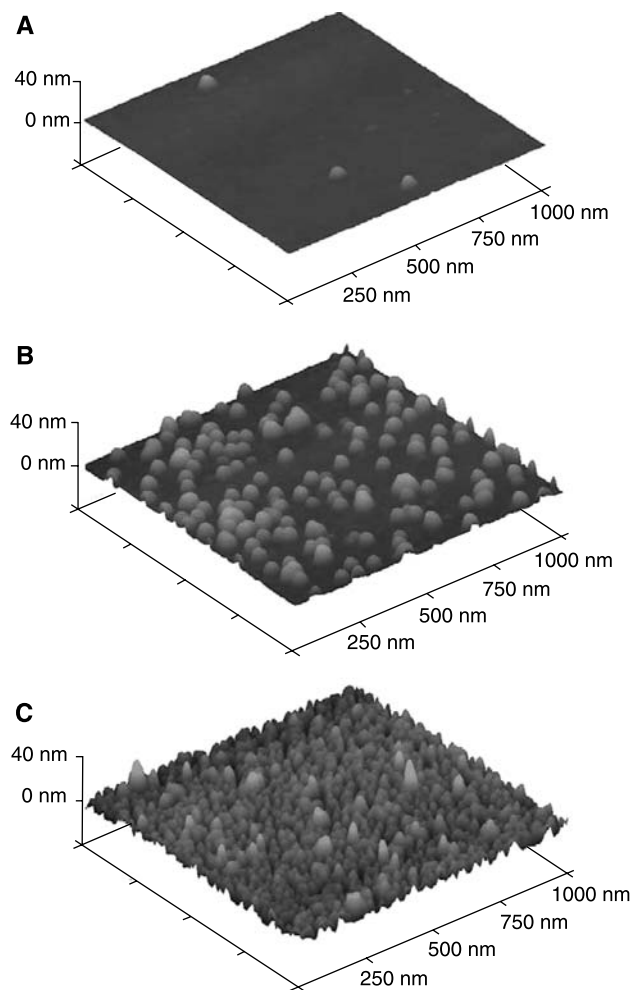


Fig. 4. AFM micrographs of the surface of *PS-co-VBT*. (A) Non-irradiated, 60 min in AuNP solution, (B) irradiated and modified with 2-aminoethanethiol, 30 min in AuNP solution, and (C) irradiated and modified with 2-aminoethanethiol, 60 min in AuNP solution

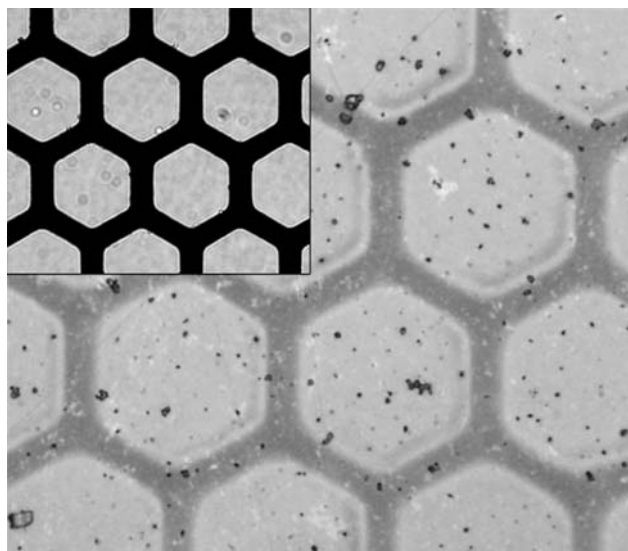


Fig. 5. Optical micrographs of a patterned gold layer at the surface of *PS-co-VBT*. The bar width of the hexagonal grid is $8\ \mu\text{m}$. Insert: micrograph of the original honeycomb TEM grid

gold coverage leads to increased reflection of light. The structures are well recognizable and a resolution of $8\ \mu\text{m}$ is achieved.

In another experiment we utilized the negative resist properties of the UV reactive polymer *PS-co-*

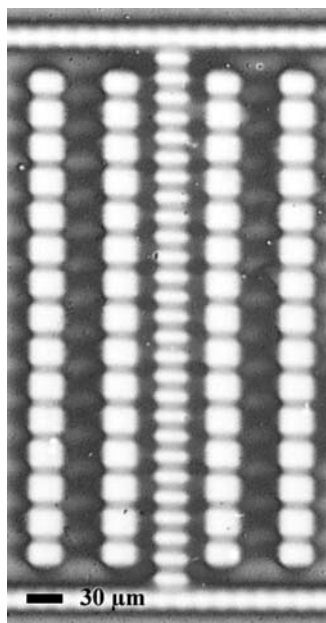


Fig. 6. Optical micrograph of a lithographically patterned layer of *PS-co-VBT* (negative image) bearing a gold layer at the surface

VBT. Upon UV irradiation, photocrosslinking *via* free radical intermediates occurs concomitantly with the described photoisomerization of SCN to NCS units. A sample of *PS-co-VBT* was illuminated using a contact mask bearing a chromium pattern on quartz. After the usual processing (reaction with 2-aminoethanethiol, immersion in AuNP solution for 15 min, and drying), the sample was developed with dichloromethane. Figure 6 shows the optical micrograph of the pattern obtained. It shows a negative pattern of photo-crosslinked *PS-co-VBT* bearing a highly reflective gold layer at its surface. We assume that the gold coverage of the UV-illuminated areas of the polymer contributes to image formation by reducing the attack of the solvent dichloromethane and thus enhances the contrast.

In conclusion, we have demonstrated the application of a photoreactive polymer, poly(styrene-co-4-vinylbenzyl thiocyanate), for the selective immobilization of gold nanoparticles at the surface. Using contact masks, gold patterns with a resolution of $8\ \mu\text{m}$ and less were achieved. Ongoing research aims at patterns with even higher (sub- μm) resolution. Moreover, inorganic surfaces equipped with self-assemblies of photoreactive molecules are currently under investigation.

Experimental

Preparation of Gold Nanoparticles (AuNP)

Prior to use, all glass equipment was cleaned by immersion in piranha solution (3 parts conc. H_2SO_4 and 1 part 33 wt% H_2O_2) and rinsing with substantial amounts of water. *Warning:* piranha solution reacts vigorously with organic matter! A solution of 0.1345 g trisodium citrate dihydrate (Sigma Aldrich, ACS) dissolved in $10\ \text{cm}^3$ deionized H_2O was added at once to a solution of 36.0 mg $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (hydrogen tetrachloroaurate(III) trihydrate, from Sigma Aldrich, >99.9%) in $100\ \text{cm}^3$ deionized H_2O while refluxing at vigorous stirring. The immediately formed colloidal gold solution (red color) was kept under reflux for further 30 min. After cooling to room temperature (20°C), the colloidal solution was filtered through a Nalgene[®] syringe filter ($0.2\ \mu\text{m}$ PTFE membrane) and stored at 4°C under exclusion of light.

Sample Preparation

For photometric measurements a 5 wt% solution of *PS-co-VBT* in anisole was spin coated onto CaF_2 discs. In a similar fashion, samples were prepared on Si wafers ($1 \times 1\ \text{cm}^2$) for AFM measurements. The film thickness amounted to approx. 100 nm. UV irradiation was carried out with the unfiltered light of a medium-pressure Hg lamp for 20 s under inert gas (N_2). The light intensity in the sample plane was measured

with a spectroscopic radiometer (Solatell Solascope). The energy density – integrated over the wavelength range 240–280 nm – was 13.3 mW cm^{-2} . For patterning, honeycomb copper grids (600 mesh; available from Ted Pella, Inc., Redding, U.S.A.) and chromium/quartz masks (test patterns; from Austria Microsystems, Unterpemstätten, Austria) were used as contact masks. For modification of the photogenerated NCS groups, the samples were immersed in a solution of 0.3 g 2-aminoethanethiol hydrochloride (Aldrich, 98%) in 25 cm^3 deionized H_2O (pH adjusted to 9.0 with NaOH). The polymer samples were kept in this solution for 120 min, taken out and rinsed carefully with deionized water (removal of physisorbed molecules). Immediately afterwards, the samples were immersed in the AuNP solution (1:1 diluted with water prior to use). The sample plates were placed in the AuNP solution with the active side (*i.e.* polymer layer) bottom down in order to prevent AuNP deposition through sedimentation. After a selected period (between 15 and 60 min) the samples were removed from this solution, rinsed thoroughly with deionized H_2O and dried *in vacuo* at 40°C .

Measurements

UV-VIS spectra were recorded with a JASCO V-530 spectrophotometer. Atomic force microscopy (AFM) was carried out with a Digital Instruments Nanoscope IIIa system operated in the tapping mode. Standard TESP tips (Tapping Mode Etched Silicon Probes) were applied. Optical micrographs were taken with an Olympus BX 60 with a magnification between $50\times$ and $1000\times$.

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