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Simple fabrication of patterned gold nanoparticle arrays on functionalized block copolymer thin films

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ABSTRACT

Patterned arrays of gold nanoparticles were fabricated using a simple dipping method that makes use of their specific interactions with nano-domains of carboxylic acid on a block copolymer template. Polystyrene-*block*-poly(*tert*-butyl acrylate) on the SU-8 photoresist pattern was selectively transformed to polystyrene-*block*-poly(acrylic acid). Au nanoparticles are selectively immobilized on the resulting carboxylic acid patterns to produce well-defined patterned Au nanoparticle arrays. This stable and robust template can be used to obtain any patterned nonaggregated metal or inorganic nanoparticle arrays.

1. Introduction

The fabrication of noble metal particle arrays of nanometer dimensions has attracted growing interest due to their utilization in several kinds of nanodevices. For the applications of the particle arrays, control over particle size, shape, and surface structure is essential, since these variables are what determine the enhanced spectroscopic properties that make these materials so useful in applications such as bio/chemosensors, optical filters, and plasmonic waveguides [1–4]. One of the key requirements in device applications is the precise positioning of nanoparticles on the substrate. Several techniques denoted as "top–down" methods have been applied toward this end, including microcontact printing, electron beam lithography, and photolithography [5–8]. However, issues such as cost and low throughput still need to be resolved.

Alternatively, a combination technique that uses both top–down and bottom–up approaches has attracted a great deal of interest for accurate, fast, and low-cost nanoparticle patterning [9,10]. The self-assembly of block copolymers is a promising technique for making nanometer-sized structures with regularly sized and spaced features, such as spheres, cylinders, and lamellae [11,12]. Preferential segregation of nanoparticles or their precursors in block copolymer microdomains has been used for patterning of nanoparticles in preferential microdomains [13,14]. However, a binary mixture of block copolymer and nanoparticles made it difficult to precisely arrive at a well-defined morphology in the resulting block copolymer composite. Otherwise, block copolymer templates can also be used as nanoreactors for the synthesis of inorganic nanoparticles. For example, quasi-hexagonally arranged nanoparticle arrays can be obtained from metal salt-loaded micellar layers of amphiphilic block copolymers [15,16], which are subsequently reduced to metal nanoparticles and patterned by electron beam lithography or focused ion-beam systems [17,18]. However, micellar approaches show limited degree of order in self-assembled nanostructures [19]. Furthermore, it cannot be used when tight control of size and shape is required to produce the desired optical properties [20].

In our previous study, we reported that polystyrene-*block*-poly(*tert*-butyl acrylate) (PS-*b*-P*t*BA) could be selectively deprotected to yield polystyrene-*block*-poly(acrylic acid) (PS-*b*-PAA) by surface silanol groups, and the resulting

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carboxylic acid groups could be formed only in the photolithographically defined region using a photocrosslinkable random copolymer film [21]. However, not only low content of photoreactive groups in the random copolymer prohibited the precise patterning process with small features, but low acidity of surface silanol groups limited effective deprotection from PS-*b*-P*t*BA to PS-*b*-PAA. The negative-tone photoresist of SU-8 is highly desirable as an acid catalyst layer due to the strong acids generated during photolysis of photo-acid generators [22]. Additionally, good patternability of SU-8 can allow selective deprotection of PS-*b*-P*t*BA in the specific region with precisely controlled pattern sizes. The resulting carboxylic acid patterns could be used as a versatile template for the patterned arrays of functional nanomaterials.

Here, we demonstrated a simple patterning method for Au nanoparticle arrays using their inherent high affinity for the PAA block of the functionalized block copolymer, PS-*b*-PAA. The block copolymer is produced from PS-*b*-P*t*BA via acid-catalyzed thermal deprotection. The deprotection reaction takes place only on the SU-8 film because it contains strong acid. Au nanoparticles are selectively immobilized on the resulting carboxylic acid patterns by the hydrogen bonding and ionic interactions [23] with Au nanoparticles covered with poly(vinyl pyrrolidone) [24,25]. Consequently, well defined Au nanoparticle arrays could be patterned on the functionalized block copolymer template through a simple dipping process. This method provides a fast, cheap, and easy way to fabricate controllable as well as reproducible patterned Au nanoparticle arrays, since it includes only dipping and rinsing steps.

2. Experimental

2.1. Materials and instrumentations

An asymmetric PS-*b*-P*t*BA diblock copolymer (M_n: 66.2 kg mol^{-1} for the PS block and 32.0 kg mol^{-1} for the P*t*BA block, PDI: 1.05) was purchased from Polymer Source Inc. and used without further purification. All chemical materials such as cyclopentanone (98%) and propylene glycol methyl ether acetate (98%) were purchased from Aldrich Chemical Company. SU-8 #25 (negative-tone photoresist) was obtained from MicroChem Corporation. The photocrosslinking was carried out by contact printing using a DUV illuminator (model 82531) from Oriel Corporation comprising of a high pressure mercury–xenon lamp. Thin film thicknesses were measured with a Gaertner L116s ellipsometer (Gaertner Scientific Corporation) equipped with a He–Ne laser (632.8 nm) at a 70° angle of incidence. IR spectra were obtained in single reflection mode using a dry N_2-purged Thermo Nicolet Nexus FT-IR spectrophotometer equipped with the smart apertured grazing angle accessory. Atomic force microscope (AFM) images were obtained with a Nanoscope IIIa multimode scanning probe microscope (Veeco) in tapping mode. Scanning electron microscope (SEM) images were recorded on a Philips XL30SFEG SEM. Oxygen-reactive ion etching (O_2-RIE) was carried out in a model of SHE-4D-20 Sam-Han Development. Dark-field scattering measurements were performed with an inverted microscope (Carl Zeizz, Axiovert 40).

2.2. Self-assembled nanostructure of PS-*b*-PAA on the patterned SU-8 film

A 1% solution of SU-8 #25 in cyclopentanone was spin-coated at 3000 rpm for 30 s to obtain a 10-nm-thick film. Pattern-wise exposure was performed on the SU-8 film with 100 mJ cm^{-2} using a deep UV exposure system. The exposed wafer was then hard-baked at 95 °C for 1 min, and the uncrosslinked SU-8 film in the unexposed areas was removed by dipping in cyclopentanone for 5 min. A 1.5% solution of PS-*b*-P*t*BA in propylene glycol methyl ether acetate was spin-coated on the patterned substrate at 3000 rpm for 60 s. The resulting 40-nm-thick block copolymer film was then annealed at 140 °C for 2 days.

2.3. Synthesis of Au nanoparticles

Au nanoparticles were synthesized according to a previously published method [20] with minor modifications. 1.0 g of poly(vinyl pyrrolidone) was dissolved in 10 mL of diethylene glycol, and the polymer solution was refluxed for 5 min. 0.5 mL of 45.9 mM H_2PtCl_6 solution was added and 1.0 mL of diethylene glycol solution containing 90 mg of $HAuCl_4$ was added to the boiling solution. The reaction mixture was allowed to reflux for 10 min. The mixture was cooled and diluted with 20 mL of ethanol. The precipitates were collected after centrifugation at 6000 rpm for 30 min, and washed with ethanol via repeated dispersion/precipitation cycles. The final products were diluted with ethanol to produce 120 mL of Solution (A), 60 mL of Solution (B), 30 mL of Solution (C), and 15 mL of Solution (D). The diameters of Au nanoparticles were 20 ~30 nm, which were comparable to the dimensions of the PAA spherical domains.

2.4. Formation of patterned Au nanoparticle arrays by a simple dipping process

The self-assembled PS-*b*-PAA thin films were dipped in the Au nanoparticle solution and then rinsed in ethanol. To optimise dipping conditions, concentration of the Au nanoparticle solution, dipping time, and rinsing time were varied. For comparison, a silicon wafer coated with PS-*b*-P*t*BA and a bare silicon wafer were also dipped in the Au nanoparticle Solution D for 20 min. For the patterned Au nanoparticle arrays, the functionalized block copolymer film on the patterned SU-8 was dipped in the Au nanoparticle Solution D for 20 min, rinsed with ethanol for 2 min. All samples were exposed to O_2-RIE for 30 s to remove organic materials. The oxygen flow rate, RF power, and pressure in the chamber were 40 sccm, 100 W, and 590 mTorr, respectively.

2.5. Dark-field scattering spectroscopy

Au nanoparticles were deposited on a bare glass slide and a glass slide coated with PS-*b*-PAA by dipping in Au nanoparticle Solution D for 20 min for dark-field scattering measurements. Samples were then illuminated by a halogen lamp using a dark-field condenser (N.A. = 1.3) with immersion oil. Light was collected through a ×43