Fabrication of optically active flexible polymer films with embedded chain-like arrays of silver nanoparticles†

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Received (in Cambridge, UK) 7th November 2007, Accepted 21st January 2008
First published as an Advance Article on the web 6th February 2008
DOI: 10.1039/b717222b

We report a straightforward method for preparation of freestanding transparent polymer film containing 2D silver nanoparticle arrays and possessing polarization-sensitive optical properties.

The preparation of ordered nanoparticle monolayers/arrays is of great interest, since they have a significant number of potential applications.[1] These include optics,[2–4] electronics,[5] sensors,[6–9] optoelectronics,[10–12] biomedical,[13–15] magnets[16,17] and storage,[18,19] to mention only a few. The next level of complexity is the fabrication of ordered nanoparticle monolayers/arrays embedded in a transparent and flexible polymeric film, which may open avenues for novel and unique applications such as miniaturized plastic optoelectronics and light-emitting devices.[20] However, the generation of ordered two-dimensional nanoparticle arrays in a polymer matrix is a challenging task. To the best of our knowledge, the straightforward approach of direct introduction of particulates into a polymer matrix by casting, spin-coating, or dip-coating typically cannot lead to a truly 2D ordered assembly embedded in a flexible polymer film. Usually, initial patterning is required before particle introduction into the film. For example, gold nanoparticle arrays were fabricated *via* a combination of polymer-on-polymer stamping and layer-by-layer polymer deposition.[21] The thickness of the array assembly in that study was around 60 nm. To this end, in this communication we describe a method for generation of freestanding polymeric film consisting of a monolayer of unidirectional ordered chain-like structures made of silver nanoparticles (Ag NP). The film is transparent, mechanically robust, flexible and exhibited polarization-sensitive optical properties. The thickness of the polymer film is 2–3 mm. Potentially the method developed may lead to 'mass production' of the optically active polymeric film employing a single nanostructured 'master'.

Recently, a novel technique for the introduction of monolayers of nanoparticles into a freestanding polymer film was reported.[22] The method consists of three consecutive steps. Firstly, the nanoparticles of interest are assembled as a monolayer on a flat substrate modified with a poly(vinylpyridine) monolayer. Next, polydimethylsiloxane (PDMS) pre-polymer is poured over the immobilized nanoparticles and left for curing. Lastly, PDMS film is peeled off the substrate, resulting in a freestanding PDMS film with embedded nanoparticles. The method reported is effective and reliable, however it is limited to fabrication of semi-ordered or disordered monolayers of nanoparticles embedded into flexible and transparent PDMS film. Here we report a next generation of the technique, where it is utilized to produce a film consisting of ordered nanoparticles structures. Specifically, a patterned PVP grafted polymer layer (polymer brush) deposited on a flat substrate was used as a 'master' to guide the particles assembly. After the ordered layer of the nanoparticles was transferred into PDMS film the 'master' could be reused to fabricate the next film.

To create the patterned PVP layer on a flat substrate the surface of a silicon wafer was modified with a monolayer of a reactive polymer. Then, part of the reactive surface created was protected by a polystyrene (PS) resist layer employing capillary force lithography (CFL)[23,24] and PVP grafting to the unprotected part of the surface at low temperatures was performed. The grafting was conducted by the 'grafting to' technique, where end-functionalized polymer molecules react with complementary functional groups located on the surface to form tethered chains. Namely, carboxy terminated PVP was anchored to the non-screened areas on the substrate at a temperature of 40 °C, which is $\sim 60^\circ$ below the glass transition temperature (T_g) of both PS and PVP. The lower temperature for the process was necessary to preserve the PS resist pattern during the grafting. The combination of CFL and low temperature polymer grafting allowed easy, large-scale surface patterning with permanently bonded polymer brushes. In this way, PVP features were created and used to self-assemble Ag NP into chain-like one-dimensional arrays that exhibit anisotropic optical properties.

For a given energy gain during attachment, the rate of the grafting is governed by kinetic factors and is substantially enhanced with increasing polymer mobility.[25] Therefore, the grafting is typically conducted from solution or polymer melt (at a temperature above T_g). To realize our patterning approach we employed a specifically designed grafting procedure, which allows chemical bonding of the polymer at high densities below its glass transition temperature. Moreover, the method allows the production of features on the level of tens and hundreds of nanometres, which has not yet been reported with the 'grafting to' method for brush anchoring.[26–28] Specifically, we have used a *solvent-assisted 'grafting to'* procedure to attach the polymer to the surface below its bulk glassy

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† Electronic supplementary information (ESI) available: Detailed experimental procedures. See DOI: 10.1039/b717222b

temperature. The polymer chains' mobility was enhanced well below T_g by saturating the deposited film with solvent from the gas (vapor) phase. Solvent vapor treatment has two effects on polymer film:[29–31] (i) a plasticization effect, which reduces the glass transition (melting) temperature; (ii) a dilution effect, which decreases the polymer layer's viscosity. These two factors enhance the polymer coils' mobility and, therefore, result in high grafting rates under mild conditions.

The general procedure for fabricating the Ag NP one-dimensional arrays is illustrated in Fig. 1. A thin layer of a polymer containing epoxy functionalities [poly(glycidyl methacrylate), PGMA, 0.07% w/v solution in $CHCl_3$] was deposited onto the surface of a silicon wafer for the initial surface modification. Recently we demonstrated that polymers possessing different functional groups (carboxy, anhydride, amino and hydroxyl) could be grafted to a surface modified with a PGMA anchoring layer.[32] Next, a thin (15 nm) PS film was deposited by dip coating (0.3% w/v, toluene) to cover the epoxy layer. To conduct CFL, a PDMS stamp was placed over the PS film and the complete assembly was annealed in an oven (30 min, 120 °C). Initial PDMS pattern periodicity was decreased twice after annealing because of the PS dewetting under the PDMS surface, as well as into the grooves of the stamp (white arrows on Fig. 2a). After annealing, the assembly was allowed to cool to room temperature before the PDMS stamp was peeled off the surface. This procedure resulted in patterning of the PS film because of selective dewetting of PS from the areas where the mold directly contacted the wafer (Fig. 2a). The entire size of the patterned area was (but not limited to) approximately 1 cm^2. It is necessary to highlight the universality of the method. In fact, various patterns can be created as long as a suitable PDMS stamp is available.

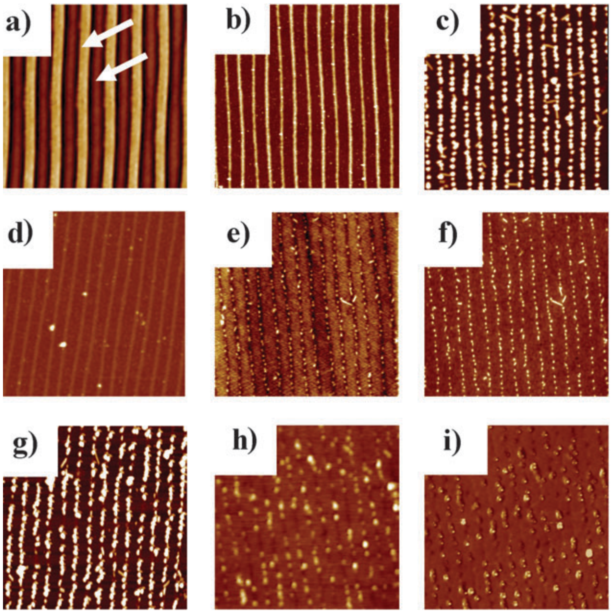

Fig. 2 AFM images (all 5 × 5 μm) of Ag NP preparation process. (a) PS CFL on the PGMA surface; (b) PVP stripes obtained *via* solvent-assisted grafting; (c) Ag NP adsorbed to PVP pattern; (d) PVP stripes after transferring of Ag NP into Sylgard matrix; (e) Ag NP embedded into polymer matrix, topography scan; (f) Ag NP embedded into polymer matrix, phase image; (g) Ag NP adsorbed to PVP stripes, second generation; (h) Ag NP embedded into polymer matrix (second generation), topography scan; (i) Ag NP embedded into polymer matrix (second generation), phase image. Scales: a,c,g,h – 50 nm; b,d,e – 10 nm; f,i – 25°.

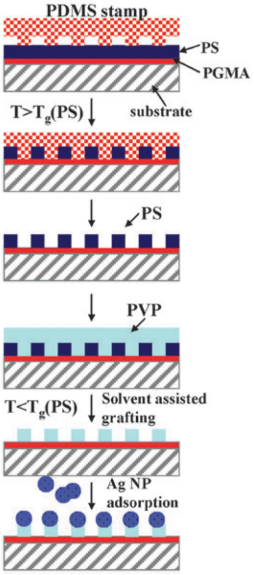

Fig. 1 Schematic diagram of Ag NP array creation process *via* solvent-assisted cold grafting.

The PS material acted as a resist protecting part of the reactive PGMA surface. Consequently, the unprotected part of the reactive layer was exposed and available for brush synthesis, whereas the remaining PS layer protected the surface from the grafting of polymer chains. Solvent-assisted grafting (40 °C, 24 h, water vapor) was then used to attach the carboxy-terminated PVP chains to the uncovered part of the surface. After the grafting was complete, the PS mask was removed with a solvent (methyl ethyl ketone, MEK), leaving the patterned PVP brush on the surface (Fig. 2b). Analysis of the AFM images gave the following parameters of the grafted PVP pattern: average distance between PVP stripes, 360 ± 20 nm; average lateral thickness of stripes, 80 nm; and height of stripes, 2 nm. Polymer thickness in the stripe corresponds to a PVP grafting density equal to 0.03 chains nm^{-2}, and the distance between grafting sites is 6.6 nm. A critical point during PVP grafting was the requirement for preserving the PS pattern on the surface. The two polymers have similar T_g[33] and it is nearly impossible to melt graft PVP without melting PS. However, solvent-assisted grafting at mild temperatures (40 °C) enabled the attachment of PVP chains and preserved the PS pattern.

The patterned PVP surface was used to assemble Ag NP (50–70 nm in size) into an array of one-dimensional chain-like structures (Fig. 2c). Toward this end, the patterned wafers were immersed in an aqueous suspension of Ag NP, causing the adsorption of NP onto the PVP chains because of this polymer's affinity to silver.[34] The average number of Ag NP particles adsorbed onto the PVP pattern, obtained from AFM image analysis, was 19.4 ± 1.5 particles μm^{-2}; and the particles' linear density on the PVP stripes was 7.3 particles μm^{-1}. Next the nanoparticle structures were transferred into PDMS resin (Sylgard 184, Dow Corning) using the procedure described elsewhere.[22] Briefly, the liquid resin was mixed with an initiator and poured onto the wafer with the assembled NP. The wafer remained in water to preserve the assembly, which would have been destroyed upon drying. After the completion of the resin polymerization, the PDMS film was pulled off the wafer with the NP assembly embedded into the transparent matrix for further optical characterization. The freestanding film produced was flexible and mechanically robust. AFM images of the Ag nanoparticles embedded in the PDMS matrix are shown in Fig. 2e and f. After the NP's removal, the patterned PVP wafer can be reused for another assembly of NP into the same one-dimensional structure. A second adsorption of the Ag NP to the 'master' and transferring to PDMS was done (Fig. 2g–i). We expect that, after the fabrication parameters are optimized, this procedure can be repeated many times to reproduce NP assemblies, using the same PVP pattern as a 'master' pattern. In particular, adsorption of the Ag NP to the already used PVP stripes can be improved with a better cleaning procedure for the PVP surface. In fact, after the first Ag NP adsorption and peeling off, some residual silver oxide layer (from the particle surface) may remain on the PVP stripes. This may decrease the affinity of the PVP master stamp to Ag NP during the following adsorptions. We expect that acid treatment followed by base treatment will clean up the PVP stamp and renew its adsorptive properties.

UV–Vis extinction spectra of the Ag NP one-dimensional structures, embedded into the PDMS transparent matrix and measured with two different light polarizations, are shown in Fig. 3. The spectra represent two films: one film was peeled from a freshly prepared PVP pattern (Fig. 3a), and the second film was templated a second time from the same master pattern. The two films exhibit quite similar polarization-sensitive spectra; however, the overall optical extinction of the second film is noticeably lower than that of the first due to the smaller number of NP particles assembled on the PVP patterned surface, as is evident from the AFM image (Fig. 2h and i). The peak in the spectra corresponds to the plasmon resonance, the frequency of which depends on the direction of the polarization of incident light relative to the orientation of the one-dimensional Ag NP assembly. The maximum at *ca.* 425 nm corresponds to the polarization vector parallel to the direction of the NP structure, whereas the maximum at 485 nm was observed with a perpendicular polarization vector. These two maxima represent two different plasmon modes: one is a longitudinal mode for which the collective electron oscillations are parallel to the structure's orientation, and the other is a transverse mode with electron oscillations perpendicular to the structure. The two modes result from the longitudinal and transverse plasmon coupling that was previously described in one- and two-dimensional Ag NP structures.[35] The Ag NP arrays' optical properties confirmed that patterning was present on a large surface area.

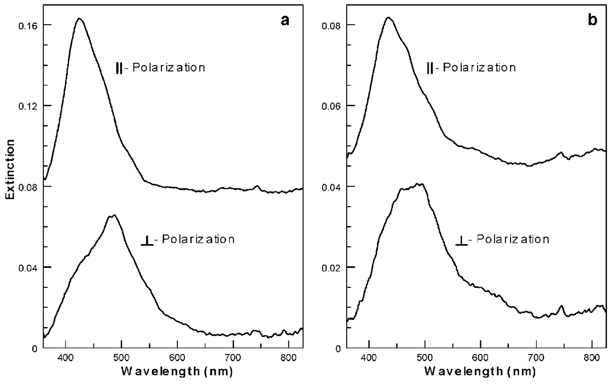

Fig. 3 UV–Vis extinction spectra of one-dimensional structure of Ag NP in the PDMA matrix on first (a) and second (b) templating.

In conclusion, we propose an easy, straightforward method for the preparation of freestanding transparent polymer film containing 2D silver nanoparticle arrays and possessing polarization-sensitive optical properties.

The authors acknowledge support by NSF grant DMR 0602528 and the ERC Program of NSF under Award No. EEC-9731680. The authors thank Dr V. Klep for the synthesis of PGMA.

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