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Hexagonally ordered nanoparticles templated using a block copolymer film through Coulombic interactions

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Abstract

We present a novel and simple method for forming hexagonal gold nanoparticle arrays that uses Coulombic interactions between negatively charged gold nanoparticles on positively charged vertically oriented poly(4-vinylpyridine) cylinders formed in a spin cast polystyrene-*b*-poly(4-vinylpyridine) block copolymer film. Exposure of the block copolymer film to dibromobutane vapor quaternizes and crosslinks the poly(4-vinylpyridine) domains which allows for the templated deposition of gold nanoparticles into a self-assembled hexagonal array through electrostatic interactions. These systems can form the basis for sensors or next generation nanoparticle based electronics.

 Online supplementary data available from stacks.iop.org/Nano/24/045305/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction

Nanoparticles show unique optical, magnetic and electric properties, which are often size or shape dependent and different from the properties of the respective bulk material [1–5]. As these properties often only emerge when appropriate phenomena of coupling and exchange between the nanoparticles exist, the nanoparticle position distribution generally needs to be controlled through immobilization and assembly of the nanoparticles on a substrate or in a medium. Recently, various polymer/nanoparticle hierarchical structures have been introduced as candidates for use in next generation applications in electronic devices and sensors [6–8]. The use of block copolymers to produce nanoscale templates

has gained increasing attention as the block copolymer morphology is determined by the volume fraction of the polymer blocks, and the size and the distance between domains is determined by the overall molecular weight [9]. Thus, block copolymers can be utilized as templates for controlling the spatial location of nanoparticles [10–12]. Among the processing techniques available for directing the self-assembly of block copolymer thin films, controlling the rate of solvent evaporation has attracted particular attention as it is simple and generally not sensitive to the substrate. An example is provided by polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) diblock copolymer having cylindrical microdomains of PEO. After solvent annealing, defect-free lateral ordering of vertically oriented PEO cylinders can be achieved over several micrometers [13]. Kim *et al* have reported a simple route for fabricating a nanopatterned array of inorganic oxide semiconductors using the PS-*b*-PEO film as a template [14]. In the film, the PEO forms hexagonally ordered domains with a ~ 2 nm depression in each of the PEO

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domains, where semiconductors such as silica and titania were grown by exposure to precursor vapor. Polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) has been used to synthesize nanoparticles by exploiting specific interactions between the P4VP block and metallic precursors [15–18]. Typically, metallic precursor loaded PS-*b*-P4VP micelles are deposited onto a substrate by spin-coating or dip coating. Subsequent plasma treatment converts the precursors to nanoparticles and eliminates the polymer; the result is a hexagonal array of nanoparticles that matches the micellar monolayer present before plasma treatment. Metal nanoparticles have been widely used as catalysts for the growth of nanowires and nanotubes [19–22], in sensors using surface enhanced Raman scattering [23, 24], and for optoelectronics [25]. However, as there was no covalent or electrostatic interaction between the plasma generated metal nanoparticles and the substrate, nanoparticle detachment from the substrate leads to the loss of the pattern [17]. In this work, we will discuss the structure of PS-*b*-P4VP films generated through solvent exposure (tetrahydrofuran (THF)) and present a simple method for generating a nanopatterned array of *ex situ* synthesized gold nanoparticles templated on the cylindrical P4VP domains by controlling the electrostatic interactions between the nanoparticles and P4VP domains. As the method does not require plasma treatment and has the merits of a ‘bottom-up’ approach, it is easy to implement, stable, reproducible and is directly suitable for large area patterning. The self-assembly using electrostatic interactions demonstrated in this work is potentially applicable to induce ordering of a broad range of negatively charged nanoparticles including magnetic nanoparticles and quantum dots.

2. Experimental details

PS-*b*-P4VP (number average molecular weight $M_n^{\text{PS}} = 47 \text{ kg mol}^{-1}$, $M_n^{\text{P4VP}} = 10 \text{ kg mol}^{-1}$, polydispersity index = 1.1), was purchased from Polymer Source, Inc., and used without further purification. PS-*b*-P4VP was dissolved in THF (Aldrich) to yield a 0.5 wt% polymer solution. The polymer solution was filtered through a Millipore 0.45 μm poly(tetrafluoroethylene) filter. The molecular size of PS-*b*-P4VP in the polymer solution was measured using dynamic light scattering (DLS). The DLS procedure was performed at 90° scattering angle and 632.8 nm wavelength using Zetasizer Nano ZS90 (Malvern Instruments Ltd). PS-*b*-P4VP films were prepared by spin-coating at 3000 rpm for 30 s on silicon substrates at different levels of relative humidity (RH). The RH during spin-coating was controlled by adding desiccant to a glass chamber enclosing the spinning chuck on which the substrate was placed. The RH was measured with a hydrometer inside the glass chamber. An alternate solvent of propylene glycol methyl ether acetate (PGMEA) was used in some experiments to scale the process up for larger substrate sizes in a clean room. For PGMAE a 0.75 wt% solution concentration was used and this was spin-coated at 2000 rpm for 30 s. As-spun films at 23% RH were annealed in THF vapor, deionized water vapor, or THF/deionized water vapor at room temperature for 6 h. Thin film surface

morphology was characterized using a Dimension 3000 atomic force microscope (AFM) from Digital Instruments, Inc. Silicon tips with spring constants ranging between 20.0 and 80.0 N m^{-1} (as specified by the manufacturer) were used. To measure the thin film thickness, the polymer films deposited on silicon substrates were scratched with a scalpel, and AFM images were taken across the borders of the scratches far enough away to ensure correct film thickness measurement. The contact angle of water on a PS-*b*-P4VP film annealed in THF vapor was measured using a Ramé-Hart Model 250-00 goniometer. 1,4-dibromobutane (DBB) was purchased from Aldrich and used without further purification. P4VP blocks in a PS-*b*-P4VP film were quaternized in DBB vapor. The degree of quaternization was measured using x-ray photoelectron spectroscopy (XPS) on a Kratos AXIS 165 x-ray photoelectron spectrometer using a monochromatic Al K α x-ray source (1486.6 eV). The instrument was operated in hybrid mode, with survey and high resolution spectra collected at pass energies of 160 eV and 20 eV, respectively. The anode voltage was 12 kV and the anode current was 20 mA. The pressure in the analysis chamber was maintained at 6.7×10^{-6} Pa or lower during each measurement. The samples were mounted on standard sample studs by means of double-sided adhesive tape. The core-level signals were obtained at a photoelectron take-off angle of 90° (with respect to the sample surface). A citrate-capped gold colloid with 15 nm mean particle diameter was purchased from BBI International. The positively charged PS-*b*-P4VP film was then immersed in a negatively charged gold nanoparticle suspension in water, thoroughly washed in deionized water and then blow dried in air. Scanning electron microscopy (SEM) observation was conducted using a Hitachi SU-70 Schottky field emission gun SEM working at 3 kV or 10 kV accelerating voltage and a working distance of approximately 5.5 mm.

3. Results

PS-*b*-P4VP with 0.175 P4VP weight fraction, which is expected to form hexagonally ordered P4VP cylinders in bulk [26], was dissolved in THF. As THF has a preferential affinity for PS compared to P4VP (reported Flory–Huggins interaction parameters $\chi_{\text{PS-THF}} = 0.35$ and $\chi_{\text{P4VP-THF}} = 0.6$) [27], PS-*b*-P4VP micelles of a PS corona and a P4VP core have been observed in THF solutions [28]. However, the micellization is highly dependent on a number of variables, such as P4VP block ratio, P4VP block molecular weight and PS-*b*-P4VP concentration [29]. Our PS-*b*-P4VP solution in THF is optically clear, and the hydrodynamic radius (R_h), obtained from the DLS measurement, is 7.5 nm, indicating that no large aggregates are formed, probably due to the low P4VP weight fraction (~ 0.175), the small M_n^{P4VP} , and the low polymer concentration. It was previously reported that for a PS-*b*-P4VP block copolymer (number average molecular weight $M_n^{\text{PS}} = 47.6 \text{ kg mol}^{-1}$, $M_n^{\text{P4VP}} = 20.6 \text{ kg mol}^{-1}$, polydispersity index = 1.14, approximately twice the P4VP block molecular weight as compared to our polymer), the R_h in a 0.5 wt% PS-*b*-P4VP/THF solution was 6 nm [27]. The

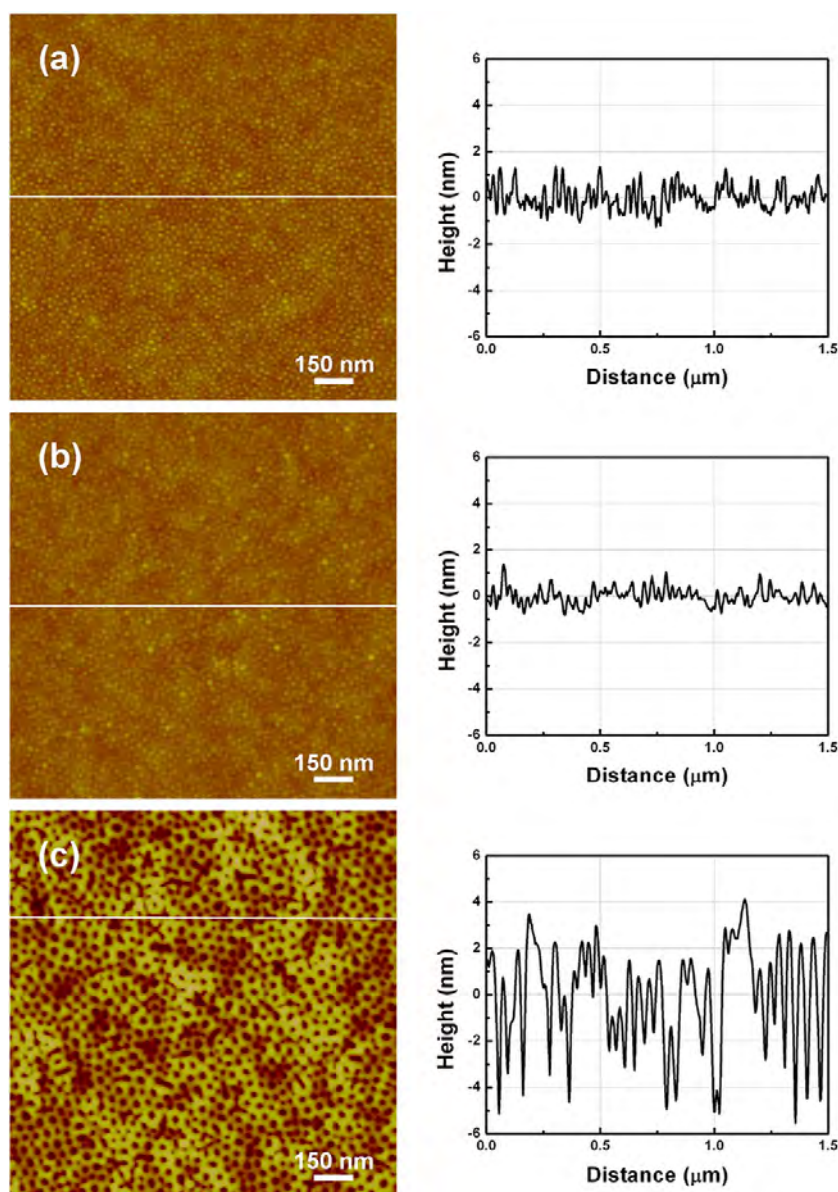


Figure 1. AFM height images of as-spun PS-b-P4VP films as a function of RH during spin-coating. RH: (a) 23%, (b) 37% and (c) 50%. All images are set to the same height scale (15 nm).

effect of the preferential affinity of THF for PS was observed in the morphologies of as-spun and THF annealed PS-b-P4VP films.

Figure 1 shows AFM height images of as-spun films depending on the RH during spin-coating. At relatively dry conditions (figures 1(a) and (b)), protruding convex nodules in a continuous matrix are observed with the nodules being less elevated at 37% RH. The observed morphologies are formed due to the differing evaporation rates of the THF in the different domains, as has been observed in as-spun films from homopolymer mixture solutions, where the solvent has a preferential affinity for one of the homopolymers [30–33]. During spin-coating of the PS-b-P4VP solutions, the THF evaporates and phase separation occurs due to the strong repulsive interaction between the blocks. Since THF prefers PS to P4VP, the P4VP domains are quickly depleted of solvent

and solidify first. Subsequent evaporation of the remaining solvent leads to collapse of the PS matrix, resulting in elevated P4VP nodules. The solvent evaporation from the surface during spin-coating leads to a reduction of surface temperature, causing condensation of water on the surface under humid conditions. As water is completely miscible with THF, this can alter the THF evaporation rate and affect the morphology of the as-spun film at high RH conditions. As shown in figure 1(c), the film spin-coated at 50% RH forms pits instead of elevated nodules for the P4VP domains. The center-to-center distance increased from 25 nm under dry conditions to 40 nm under humid conditions. The condensed water would be distributed within the hydrophilic P4VP domains, and make P4VP chains swell. The P4VP domains solidify last after the complete evaporation of the THF and condensed water, leading to an elevated PS matrix. A similar

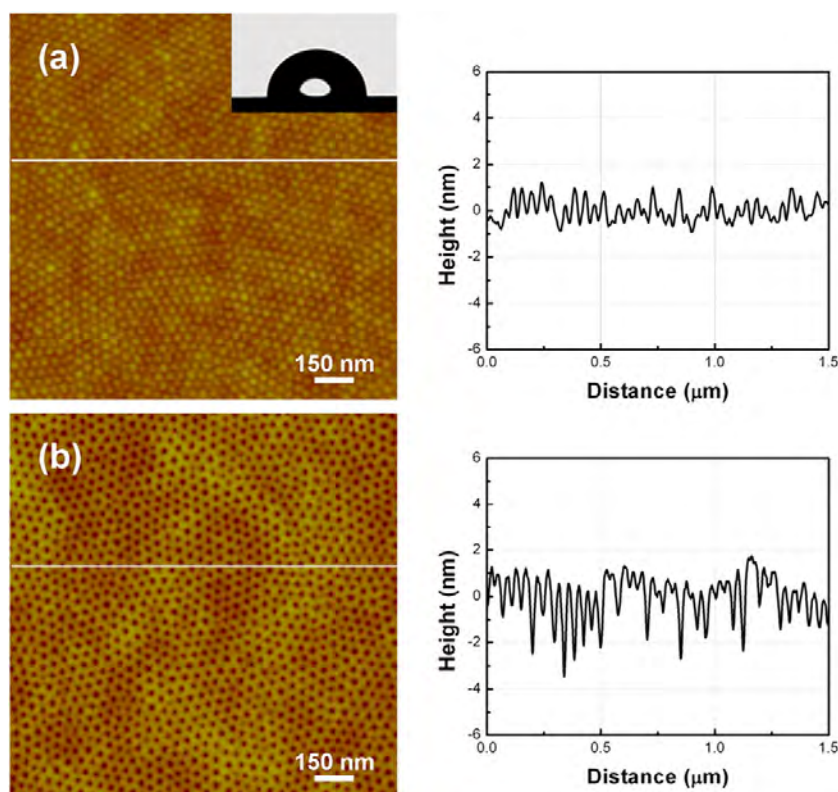


Figure 2. AFM height images of PS-b-P4VP films annealed in (a) THF and (b) THF/deionized water (50/50 v/v). All images are set to the same height scale (15 nm).

effect of humidity during spin-coating on the morphologies of as-spun PS/poly(2-vinylpyridine) (P2VP) blend films [34] and PS-b-P2VP micelle films [35] has been observed.

As high RH is often undesirable for manufacturing, the as-spun film fabricated at relatively low RH (23%) was chosen and annealed in THF vapor for 6 h at room temperature to induce a high degree of lateral ordering; an AFM height image of the THF annealed PS-b-P4VP film is shown in figure 2(a). The film annealed in THF vapor shows a long-range hexagonally ordered structure with a center-to-center distance, 41.5 nm, indicating reorganization of the PS-b-P4VP film structure through THF annealing. The high degree of lateral ordering is beneficial for nanotemplating applications. The annealed PS-b-P4VP film may have either a micellar structure with only PS exposed to the air surface or a structure of hexagonally arranged P4VP cylinders in a PS matrix with both blocks exposed to the air surface. In the literature there are conflicting reports on the structure of PS-b-P4VP films generated through THF annealing. Although mean field calculations have shown that hexagonally packed P4VP cylinders embedded in PS are expected for a volume fraction of P4VP block ranging from 0.12 to 0.31 [26], the morphology observed in this work might be a PS-b-P4VP spherical micelle film. On the basis of a plan view TEM image of a THF annealed PS-b-P4VP film after I_2 staining, Yun *et al* have reported that when a PS-b-P4VP (number average molecular weight $M_n^{PS} = 47.6 \text{ kg mol}^{-1}$, $M_n^{P4VP} = 20.6 \text{ kg mol}^{-1}$, polydispersity index = 1.14) micelle film was annealed in THF, the hexagonal order was improved but the film remained

composed of micelles with a PS corona and a P4VP core. The improved ordering occurred as PS-b-P4VP chains were exchanged between micelles [36]. However, Park *et al* have reported two different thin film structures of PS-b-P4VP films after THF annealing using a PS-b-P4VP polymer (number average molecular weight $M_n^{PS} = 47.6 \text{ kg mol}^{-1}$, $M_n^{P4VP} = 20.6 \text{ kg mol}^{-1}$, polydispersity index = 1.14): one is a hexagonally ordered PS-b-P4VP micelle film [37, 38] and the other is hexagonally ordered cylindrical PS-b-P4VP in a PS matrix with a depression in each P4VP domain [39, 40]. These two morphologies are not distinguishable by AFM, as both can result in elevated domains with circular cross-section (figure 2(a)). It was reported that after a PS-b-P4VP/small molecule supramolecular assembly film was annealed in THF vapor, hexagonally ordered P4VP cylinders containing small molecules in a PS matrix were generated where each P4VP cylindrical domain was elevated [41]. The mechanism originally proposed for solvent annealing is that the gradient of the solvent evaporation rate in the direction vertical to the substrate leads to vertically oriented block copolymer structures. A critical difference between a PS-b-P4VP spherical micelle film and a PS-b-P4VP vertically oriented cylinder film relates to whether the P4VP domains are exposed to the air surface. In a PS-b-P4VP micelle film with a PS corona, the surface of the film should be only PS with no P4VP exposed. In order to verify the film structure in figure 2(a), we measured the contact angle for water on the THF annealed film, and a typical result is shown in figure 2(a) as an inset. To increase the accuracy of the measurements,

six different positions were measured. The contact angle for water on the annealed PS-*b*-P4VP film was on average 83.3°, which is less than the contact angle (90°) for water on a PS film and larger than the contact angle (75.6°) for water on P4VP film [42]. The contact angle for water on an as-spun PS-*b*-P4VP spherical micelle film was reported to be 105°, higher than observed for a pure PS film [43]. Our result indicates that hydrophilic P4VP domains in the THF annealed PS-*b*-P4VP films are exposed to the air surface and the film structure is vertically oriented P4VP cylinders.

The film thicknesses of the as-spun film and the annealed film were 25 nm and 24 nm, respectively. The as-spun film was gray in color. During annealing in THF vapor, the color of the film changed and eventually remained yellow, indicating that the film thickness increased due to swelling with THF. When the film was removed from the THF vapor, the film color quickly turned gray as the THF evaporated. This process is very similar to what happens during spin-coating from THF solution. The resulting P4VP domains in the THF annealed films are also elevated, as is observed in the as-spun films. When PS-*b*-P4VP films are annealed in THF vapor, it is likely that self-assembly occurs at the air surface and ordering then propagates through the film, resulting in elevated P4VP domains. To verify this, we attempted to invert the surface structure of our PS-*b*-P4VP film by annealing the as-spun PS-*b*-P4VP film fabricated at the low RH conditions (RH: 23%) in THF/water vapor. When it was exposed to vapor from a 50:50 v/v THF/water mixture, the as-spun film turned yellow as the PS-*b*-P4VP film swelled. When PS-*b*-P4VP films are swollen with THF, water vapor can dissolve into the films as water is completely miscible with THF and can hydrogen bond to the P4VP block. An AFM height image of the THF/water annealed film is shown in figure 2(b). While the film annealed in THF/water vapor formed a hexagonally ordered PS-*b*-P4VP cylindrical structure, the P4VP domains became pits, in contrast to the THF annealed film case, indicating that dissolved water altered the THF evaporation rate in the P4VP domains. It is notable that the center-to-center distance between P4VP cylinders increased from 41.5 nm to 47 nm. Although it is unknown whether the center-to-center distance between P4VP domains at the surface of the PS-*b*-P4VP film annealed in THF/water vapor is maintained throughout the entire thickness, we believe that dissolved water swelled P4VP domains as observed in figure 1(c), giving rise to the change in the center-to-center distance. For comparison, the as-spun film was also annealed in water vapor. When the as-spun film was annealed in water vapor, its color did not change, indicating no change in the film thickness as water is a non-solvent for our PS-*b*-P4VP. The surface morphology of the annealed film is identical to that of the as-spun film (figure 1(a)), as expected. (See supporting information, figure S1 available at stacks.iop.org/Nano/24/045305/mmedia.)

The above results suggest that the film morphology is a hexagonal structure of P4VP cylinders in a PS matrix grown via directional solvent evaporation. As the hexagonally ordered P4VP domains generated by THF or THF/water annealing are exposed to the air surface, the domain structure

can be used to control the positioning of nanoparticles on the basis of selectivity of surface interactions. As the THF annealed film showed better ordering and regularity in P4VP domain size, the THF annealed PS-*b*-P4VP film was selected for use as a template. P4VP domains in the THF annealed film were first quaternized to allow the generation of an ordered nanoparticle array via Coulombic interactions of the negatively charged gold nanoparticles with positively charged quaternized P4VP domains. P4VP quaternization (and crosslinking) was accomplished by exposing the film to dibromobutane (DBB) vapor [44]. After quaternization, the film was washed with hexane and dried in air. The film structure was maintained after quaternization, as confirmed using AFM (as shown in figures S2 and S5 in the supporting information available at stacks.iop.org/Nano/24/045305/mmedia).

To verify P4VP quaternization, the quaternized PS-*b*-P4VP film was characterized using XPS and the result was compared to an unquaternized PS-*b*-P4VP film, as shown in figure 3(a). To compensate for surface charging effects, all core-level spectra were referenced to the C 1s hydrocarbon peak at 284.8 eV. The N 1s core-level spectrum of the untreated PS-*b*-P4VP film (black line) indicates a peak at 399.4 eV attributed to the nitrogen in the pyridine group. After quaternization, the N 1s core-level spectrum (red line) shows an additional XPS peak at a binding energy above 402 eV, attributable to the positively charged nitrogen [46]. The N 1s region was fit to two peaks with a 70%/30% Gaussian/Lorentzian product function of equal full width at half-maximum after application of a Shirley background. The degree of quaternization of the pyridine groups was calculated to be 66%.

The evolution of an ordered array of gold nanoparticles on the quaternized PS-*b*-P4VP thin film was followed using SEM as shown in figures 3(b)–(f). To show the underlying block copolymer pattern, the contrast and brightness of the right half of figure 3(b) were enhanced. P4VP domains appear slightly brighter compared to the PS matrix due to elevation. As shown in figure 3(b), the hexagonally ordered block copolymer structure is maintained after the quaternization and self-assembly. The gold nanoparticles are located exclusively on the P4VP domains in the quaternized films, indicating that the self-assembly was driven by electrostatic interactions. Since the gold nanoparticles are not forced to sit on the center of each quaternized P4VP domain, the regularity of the center-to-center distance between gold nanoparticles is less than the underlying block copolymer pattern although they show the same average value.

The nanoparticle/block copolymer site coverage was calculated from the SEM images as a function of immersion time. Here, the site coverage is defined by the average number of gold nanoparticles over the average number of P4VP domains. The average number of gold nanoparticles in a 0.5 μm^2 area was calculated from the SEM images using ImageJ software [47]. To increase accuracy, at least four different SEM images per immersion time were analyzed. When a nanoparticle pair was observed on a P4VP domain, it was counted as a single particle. The average number of

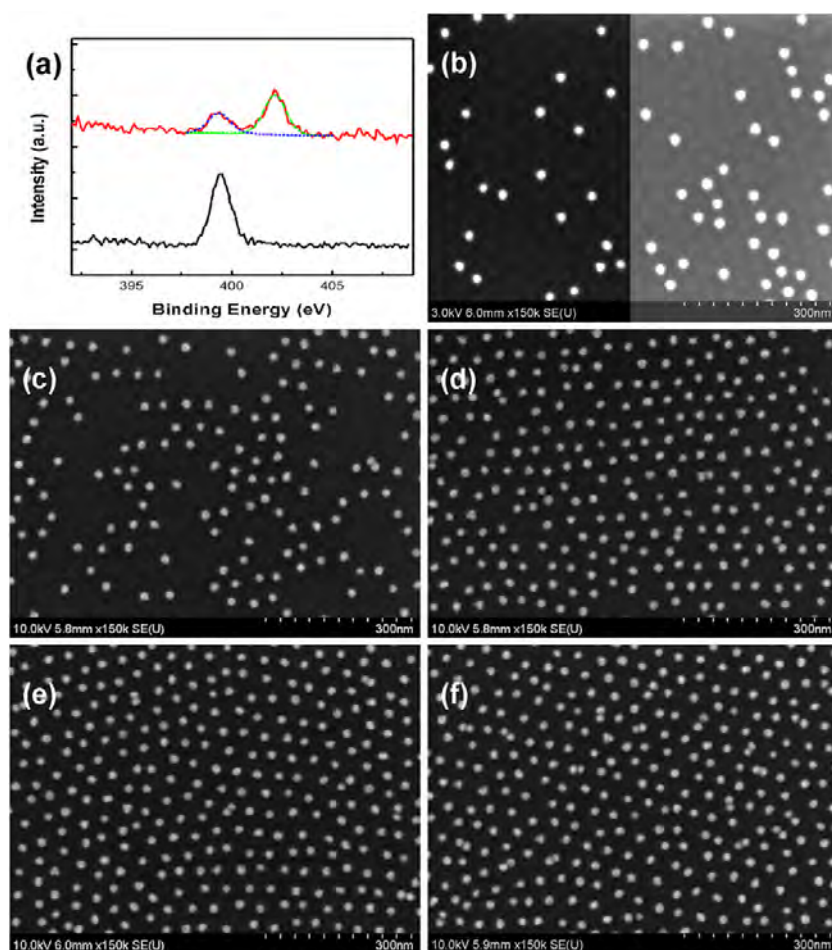


Figure 3. (a) XPS N 1s core-level spectra of PS-b-P4VP film before (black line) and after (red line) quaternization (supporting information from [45]). For clarity, the red line was shifted vertically. SEM images of gold nanoparticles on the quaternized PS-b-P4VP film as a function of immersion time: (b) 5 min, (c) 20 min, (d) 1 h, (e) 3 h and (f) 6 h.

P4VP domains per $0.5 \mu\text{m}^2$ was counted from four different SEM images of the quaternized PS-b-P4VP films without gold nanoparticles. The average number of P4VP domains per $0.5 \mu\text{m}^2$ was 322. This value is close to 355, which is the number of P4VP domains per $0.5 \mu\text{m}^2$ calculated from the measured center-to-center distance (41.5 nm) between P4VP domains assuming an ideal hexagonal structure. The results are summarized in figure 4. The site coverage rapidly increases at the early stage and then plateaus as the immersion time increased. Almost all P4VP domains (about 97%) were decorated with gold nanoparticles within 3 h. Immersion for longer than 3 h did not change the site coverage, but the fraction of nanoparticle pairs increased from 0.01 to 0.035. Some quaternized P4VP domains can accommodate more than one nanoparticle, depending on how far displaced from the center of the P4VP domain the first nanoparticle is immobilized. The ratio of pairs to unimers could potentially be controlled by varying the ratio of the domain to nanoparticle size.

To scale up the fabrication process to large area substrates, the process was performed in a cleanroom facility, and the polymer was dissolved in PGMEA instead of THF. PGMEA is a widely used clean room solvent with low health and environmental impacts. PGMEA is also a relatively

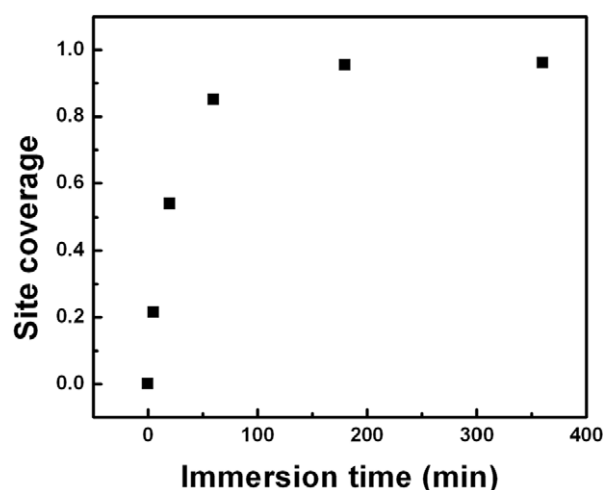


Figure 4. Site coverage of block copolymer thin films with gold nanoparticles as a function of immersion time.

slowly evaporating solvent, which enables solution dispensing over large wafers with uniform film thickness control through spin-coating. Using PGMEA the fabrication process has been extended to 4'' wafers, which is the upper limit of the facility available at the University of Maryland.

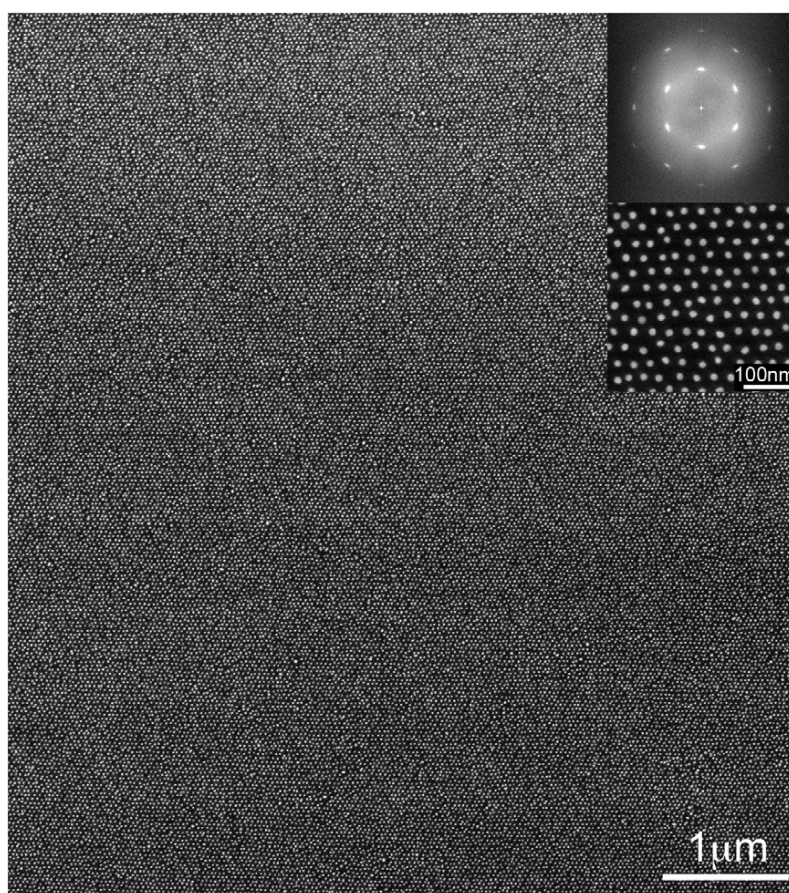


Figure 5. SEM micrographs taken from a four-inch wafer sample spin cast from PGMEA showing a large gold nanoparticle array domain. The top inset is an FFT of approximately $100 \mu\text{m}^2$ and the lower inset shows a higher magnification SEM micrograph. The average domain size in the films is approximately $100 \mu\text{m}^2$.

The process resulted in a uniform hexagonal array of gold nanoparticles on the entire wafer. Figure 5 shows an SEM micrograph of part of a hexagonally ordered gold nanoparticle array approximately $100 \mu\text{m}^2$. The top inset fast Fourier transform (FFT) is from the entire $100 \mu\text{m}^2$ domain in the original SEM micrograph, indicating that the ordering extends over relatively large areas. Off the edge of the image in figure 5 are other domains with different orientations. A boundary area between two domains is shown in the supporting information (figure S6 available at stacks.iop.org/Nano/24/045305/mmedia). Both low and high angle change in pattern orientation across the boundary can be observed in figure S6 (available at stacks.iop.org/Nano/24/045305/mmedia). Over the area of a single domain the hexagonal orientation is uniform, as demonstrated by the single-crystal-like FFT pattern inset in figure 5. Although the orientation is uniform within a domain there are defects within the pattern. The average major defect density was found to be about 4 defects/ μm^2 , where major defects are defined as nanoparticle pairs, large nanoparticles, or site vacancies. Nanoparticles that were slightly deviating from their ideal position were not considered major defects.

It should be noted that the number of defects is also affected by the quality of gold colloid solution which can contain large nanoparticles and aggregated nanoparticle pairs. As noted, the gold colloid solution was purchased from

BBInternational and while it has a relatively uniform size distribution (the polydispersity is less than 5% as measured using small angle x-ray scattering), there can be some aggregation with aging or variability between batches.

The optical properties of the gold nanoparticle arrays on coated glass and silicon have been reported in a separate paper [45].

In comparison to methods that transfer block copolymer self-assembled patterns into substrates via plasma etching [48, 49], or growing functional moieties within the self-assembled block copolymer structure by either sequential infiltration [50] or traditional liquid phase reactions [10, 51], using Coulombic interactions to attach the nanoparticles to the polymer film is relatively simple and can potentially template nanoparticles that are larger than the domain size. In comparison to nanoparticle patterning through micelles and plasma processing [15–18], block copolymer patterning provides potentially improved ordering and more flexibility in the kinds of nanoparticles that can be patterned.

4. Conclusions

In conclusion, we have demonstrated control over surface morphologies of PS-*b*-P4VP films prepared through spin-coating and solvent annealing. Since the block copolymer self-assembly occurs at the air surface and ordering

then propagates through the film, a hexagonally ordered PS-b-P4VP morphology, oriented normal to the substrate, was obtained. The PS-b-P4VP film showed elevated P4VP domains due to the preferential affinity of THF for PS. The quaternization of the pyridine groups in these PS-b-P4VP films was demonstrated. The quaternized films were used to induce the templating of a hexagonal gold nanoparticle array with high fidelity through electrostatic interactions. The self-assembly protocol was carried out completely in solution and is expected to be applicable for inducing ordering of other negatively charged nanoparticles. The process can be easily scaled to large substrates and we have demonstrated scaling to 4" wafers with single-crystal domain sizes of approximately 100 μm^2 . Such nanoparticle arrays can potentially be used for sensing [45] and nanoparticle-based electronics and data storage.

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Supporting information

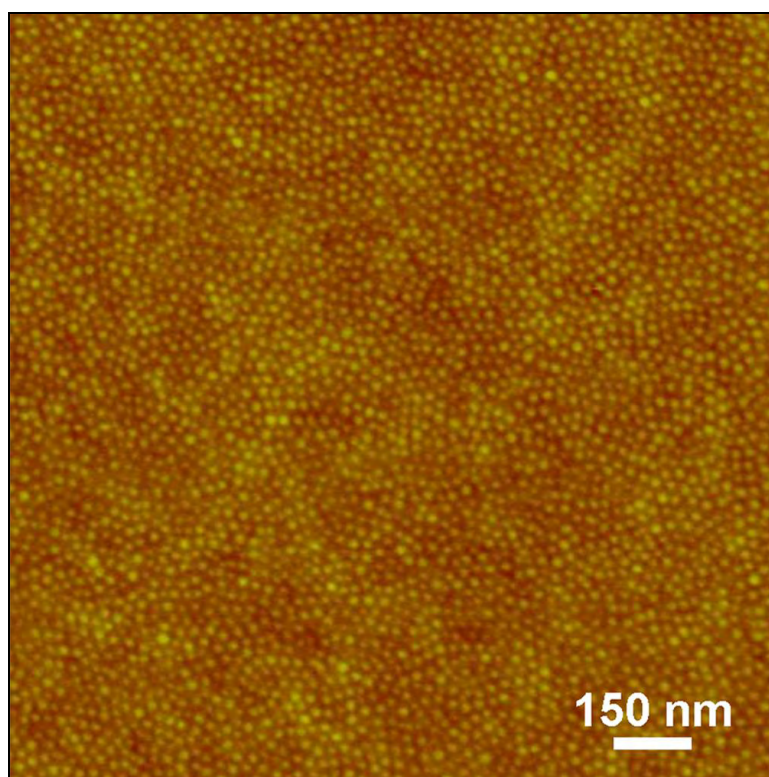


Figure S1. AFM height image of a PS-b-P4VP film annealed in water vapor.

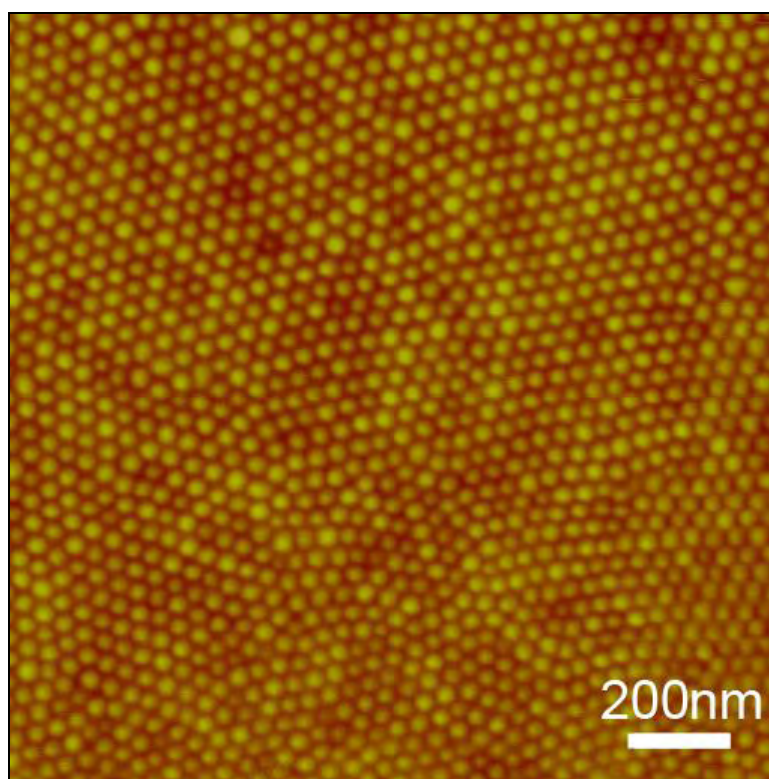


Figure S2. AFM height image of a PS-b-P4VP film after DBB crosslinking.

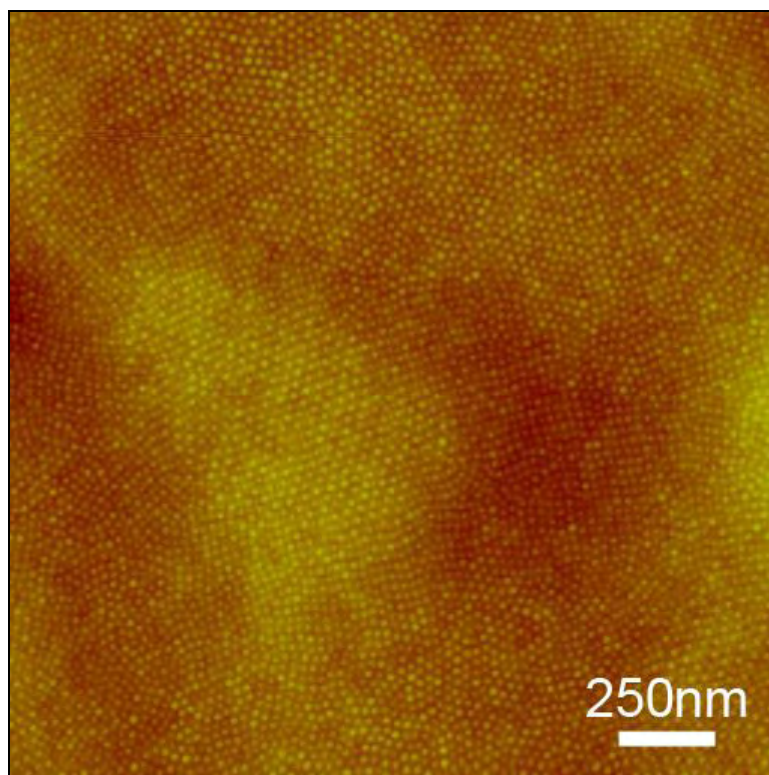


Figure S3. AFM height image of a PS-b-P4VP spin cast from 0.75 wt. % solution in PGMEA at 2000 rpm for 30 seconds, as-spun morphology.

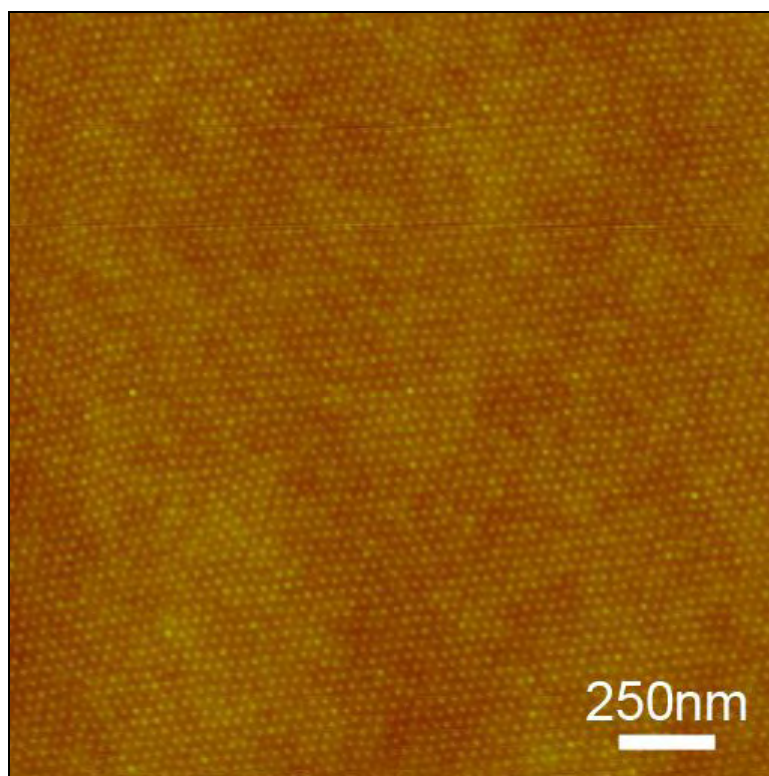


Figure S4. AFM height image of a PS-b-P4VP spin cast from PGMEA exposed to THF vapor.

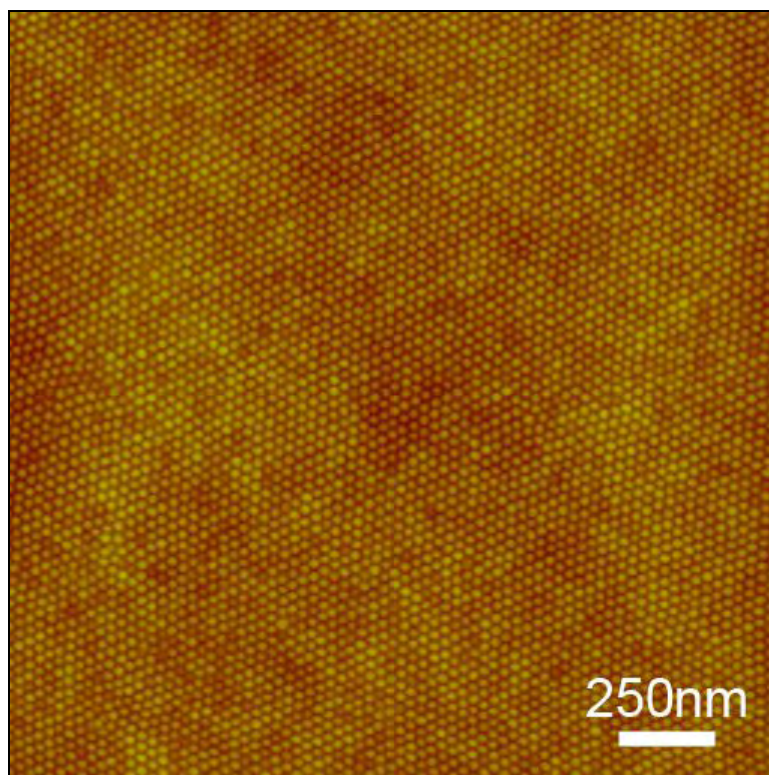


Figure S5. AFM height image of a PS-b-P4VP spin cast from PGMEA solution after DBB crosslinking.

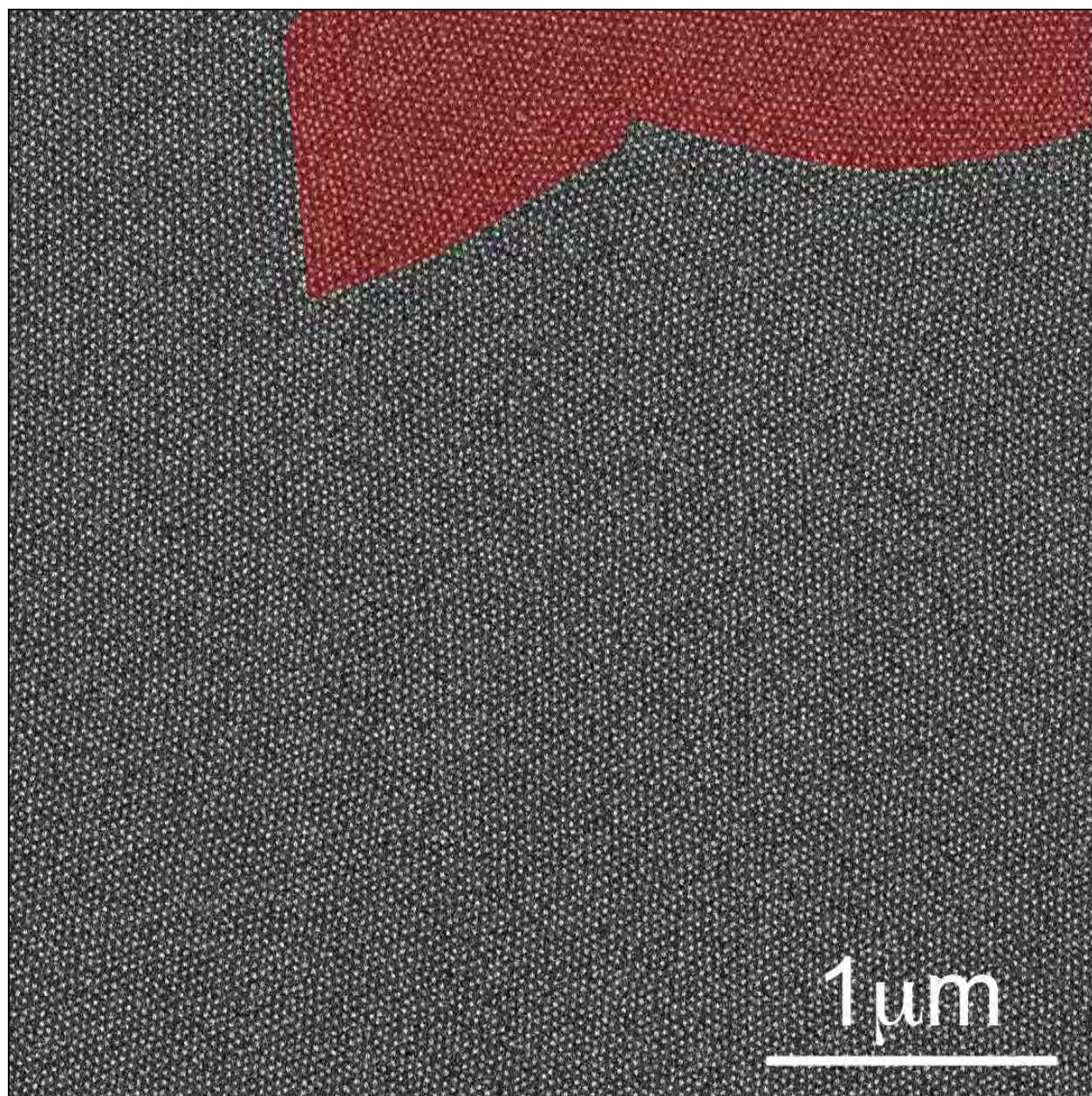


Figure S6. SEM micrograph showing grain boundary as indicated by red overlayer.