

# Gold Nanoparticles Grown on Star-Shaped Block Copolymer Monolayers

Rattanon Suntivich,<sup>†</sup> Ikjun Choi,<sup>†</sup> Maneesh K. Gupta,<sup>†</sup> Constantinos Tsitsilianis,<sup>‡</sup> and Vladimir V. Tsukruk<sup>\*,†</sup>

<sup>+</sup>School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332-0245, United States

<sup>†</sup>Department of Chemical Engineering, University of Patras, 26504 Patras, and Institute of Chemical Engineering and High Temperature Processes (FORTH/ICE-HT), Greece

Supporting Information

**ABSTRACT:** We report on the growth of gold nanoparticles in polystyrene/poly(2-vinyl pyridine) (PS/P2VP) star-shaped block copolymer monolayers. These amphiphilic  $PS_nP2VP_n$  heteroarm star copolymers differ in molecular weight (149 000 and 529 000 Da) and the number of arms (9 and 28). Langmuir—Blodgett (LB) deposition was utilized to control the spatial arrangement of P2VP arms and their ability to reduce gold nanoparticles. The  $PS_nP2VP_n$  monolayer acted as a template for gold nanoparticle growth because of the monolayer's high micellar stability at the liquid—solid interface, uniform domain



morphology, and ability to adsorb Au ions from the water subphase. UV–vis spectra and AFM and TEM images confirmed the formation of individual gold nanoparticles with an average size of  $6 \pm 1$  nm in the P2VP-rich outer phase. This facile strategy is critical to the formation of ultrathin polymer–gold nanocomposite layers over large surface areas with confined, one-sided positioning of gold nanoparticles in an outer P2VP phase at polymer–silicon interfaces.

## INTRODUCTION

The growth of metal nanoparticles on organic, biological, and polymeric templates under ambient conditions is a versatile approach to the formation of organic—inorganic nanocomposites.<sup>1–11</sup> Nanocomposites containing gold nanoparticles have a strong potential to be useful in many future applications in areas such as electronic devices, sensors, catalysts, and cancer therapy.<sup>12-15</sup> Among recent examples of polymeric templates for inorganic nanoparticle formation are histidine- and tyrosine-rich proteins and synthetic amino acids for titania and gold nanoparticle formation on organic films via plasma-enhanced chemical vapor deposition.<sup>16,17</sup> Additionally, a polystyrene-polyvinylpyridine block copolymer (PS-b-PVP) and 2-(4'-hydroxybenzeneazo)benzoic acid (HABA) have been used to facilitate nanotemplates and control the orientation of metals such as Ni nanodots and nanowires.<sup>18</sup> Poly(vinylpyridine) (PVP) is widely used to synthesize nanoparticles by itself as well as in combination with other polymers.<sup>19</sup> However, block copolymers with the ability to form stable micelles in solution and at interfaces are excellent candidates for the preparation of gold nanoparticles with a narrow size distribution and long-term stability.<sup>20</sup>

Polystyrene-*block*-poly(2-vinyl pyridine) (PS-*b*-P2VP) is a block copolymer commonly explored for gold nanoparticle preparation because the pyridine functional group in P2VP can stabilize AuCl<sub>4</sub><sup>-</sup>, which is a gold nanoparticle precursor. Adding a chemical reducing agent or using UV irradiation will reduce the complex metal ion. The reduction causes metal atom formation, aggregation of the clusters, and finally the growth of gold nanoparticles.<sup>21</sup>

The size and distribution of metal nanoparticles grown on polymeric templates can be changed by many factors such as the initial molar ratio of the metal to the amine groups, the film thickness, and the temperature. The amine groups in polymer chains can serve to bind gold ions and stabilize gold nanoparticles. Therefore, gold nanoparticles can be formed with a narrow size distribution at a high amine to gold ion ratio. $^{22-24}$  The film thickness and temperature affect the size and shape of the gold nanoparticles when synthesized by the thermal decomposition of HAuCl<sub>4</sub> in a solution of linear PS-b-P2VP copolymers.<sup>25</sup> Also, the size of the gold nanoparticles increases significantly when synthesized in thicker polymer films. Unfortunately, nanoparticles that are synthesized at a lower temperature possess a wide size distribution because of the slow reaction that leads to poorly controlled nucleation and growth.<sup>26-28</sup> Moreover, even if the growth of gold nanoparticles was extensively studied for bulk PVP-containing materials the nanoparticle reduction ability in ultrathin films such as monomolecular layers is rarely explored.

Linear PS-*b*-P2VP forms micelles with a P2VP core in toluene and can be used as templates to synthesize gold nanoparticles by mixing HAuCl<sub>4</sub> in the solution and subsequently adding a reducing agent.<sup>29</sup> In this approach, the size of the gold particles is controlled by the concentration of the gold precursor. In addition, the stability of individual gold nanoparticles depends on

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Table 1. Molecular Characteristics of PS<sub>n</sub>P2VP<sub>n</sub> Heteroarm Star Copolymers<sup>60</sup>

	numb	er of arms	PS		P2VP			
composition	$N^{a}$	total <sup>b</sup>	$M_{ m w}^{\ c}$	${N_{\mathrm{PS}}}^d$	$M_{ m w}^{\ e}$	$N_{\mathrm{P2VP}}{}^{f}$	$\Phi_{ ext{P2VP}}{}^{g}$	$M_{ m w, \ tot}{}^h$
PS <sub>9</sub> P2VP <sub>9</sub>	9	18	3400	33	13 200	126	0.8	149 000
$\mathrm{PS}_{28}\mathrm{P2VP}_{28}$	28	56	3000	29	16 000	152	0.84	529 000

<sup>*a*</sup> Numbers of PS and P2VP arms. <sup>*b*</sup> Total number of arms for an individual star copolymer including the PS and P2VP arms. <sup>*c*</sup> Weight-average molecular weight of a single PS arm. <sup>*d*</sup> Degree of polymerization of a single PS arm. <sup>*c*</sup> Weight-average molecular weight of a single P2VP arm. <sup>*f*</sup> Degree of polymerization of a single star copolymer. <sup>*b*</sup> Total weight-average molecular weight of the star copolymer.

the stability of the micelle template. However, linear block copolymers do not excel in precisely controlling the size of the nanoparticles formed and their aggregation.<sup>30</sup> In particular, the low stability of the micelle template in solution is a major challenge in using linear block copolymers. Linear PS-*b*-P2VP cannot form spherical nanoparticles if the block copolymer concentration is below the critical micelle concentration, and their poor stability leads to the growth of irregular gold nanoclusters in solution and on solid substrates.<sup>31,32</sup>

Branched polymers such as dendrimers, hyperbranched polymers, and star-shaped block copolymers with distinct supramolecular structures have also been widely investigated as templates for inorganic nanoparticle formation.<sup>33–38</sup> Dendrimers and functionalized hyperbranched macromolecules have been demonstrated to be peculiar ultrathin templates for nanoparticle formation such as nanofibrillar discrete spherical particles, interconnected ring-shaped particles, and structures.<sup>36,39,40</sup> The advantage of the highly branched polymers is their stability due to the covalent bonds between core segments.<sup>41</sup> A star copolymer is one type of branched polymer that has unique morphology and a lower aggregation number.<sup>42</sup> In addition, star polymers remain solvent-responsive and can be synthesized to have a narrow size distribution.<sup>43–45</sup> Star-shaped PS-P2VP block copolymers can be utilized as a robust template for the formation of gold nanoparticles in the solution state.<sup>20,30</sup> In toluene, 5 nm gold nanoparticles can be synthesized inside star PS-P2VP molecule having PS-b-P2VP diblock arms to form a hydrophilic P2VP core and a PS shell structure. Minko et al. demonstrated the metallization of different arms for adsorbed PS<sub>n</sub>P2VP<sub>n</sub> heteroarm star copolymers.<sup>46,47</sup>

In recent studies, various linear and star P2VP macromolecules in the inner cores of micelles were used as a template for the synthesis of gold nanoparticles.<sup>2,9,35,37</sup> However, there is no report of gold nanoparticle synthesis with P2VP chains acting as an outer phase. The synthesis of gold nanoparticles within the P2VP thin outer layer instead of the inner P2VP cores offers an opportunity to explore a new route toward the synthesis of ultrathin nanocomposite films with a one-sided confinement of gold nanoparticles.

In this study, we demonstrate the gold nanoparticle synthesis at the liquid—solid interface by using an amphiphilic  $PS_nP2VP_n$ heteroarm star block copolymer with a P2VP phase forming an outer layer in the film. We revealed how the number of arms and the chain conformation of star copolymers affect the nanoparticle dimensions. The  $PS_nP2VP_n$  Langmuir—Blodgett (LB) monolayer fabricated here acted as a template for gold nanoparticle growth because of its uniform domain structure with high stability at the air—water interface and LB monolayer. UV—vis spectroscopy, atomic force microscopy (AFM), and transmission electron microscopy (TEM) have all been used to confirm the formation of gold nanoparticles with an average size of 6  $\pm$  1 nm on the P2VP-rich side of the interface.

# EXPERIMENTAL SECTION

Materials and Substrates. Amphiphilic PS<sub>n</sub>P2VP<sub>n</sub> heteroarm star copolymers were synthesized by the "in-out" method through anionic "living" polymerization in a multistep one-pot reaction as described previously.<sup>48</sup> Briefly, linear PS chains were prepared by reacting styrene with BuLi to generate living PS chains in THF at low temperature (< -40 °C). Next, the living linear chains were cross-linked by adding divinylbenzene (DVB) as a cross-linker to generate living  $PS_n$ star polymers with polyDVB cores bearing active sites equal to the attached PS arms. In the last step, 2VP was added in the reaction to form the second generation of arms. P2VP chains grow from the polyDVB core and complete the synthesis process. The polymers were precipitated in MeOH, dried under vacuum, redissolved in benzene, and freeze dried. All PS<sub>n</sub>P2VP<sub>n</sub> heteroarm star copolymers were characterized by gel permeation chromatography, <sup>1</sup>H NMR, and light-scattering techniques.<sup>48</sup> The molecular characteristics are summarized in Table 1, and the chemical structures and schematics are presented in Figure 1A.

HAuCl<sub>4</sub> (99.99% trace metals basis) solution and sodium citrate (99 wt %) were purchased from Sigma-Aldrich. [100] silicon substrates and glass substrates were cut freshly in  $1 \times 2 \text{ cm}^2$  pieces. Piranha solution (3:1 concentrated sulfuric acid/hydrogen peroxide) was used to clean the substrate according to the normal procedure.<sup>49–51</sup> (*Caution! Piranha solution is hazardous.*) Consequently, the silicon substrates were rinsed with Nanopure water (18.2 M $\Omega$  cm) and dried with a stream of dry nitrogen.

**Fabrication of the Langmuir**–**Blodgett Monolayers.** PS<sub>n</sub>P2VP<sub>n</sub> monolayers have been prepared on silicon substrates with the LB technique.<sup>52,53</sup> We utilized a KSV2000 minitrough at room temperature according to the normal process. The star polymers were dissolved in a nonselective solvent (90/10 vol/vol chloroform/methanol) with a concentration of 0.001–0.1 mg/mL. The LB minitrough was filled with Nanopure water at pH 6. The silicon substrate was submerged in a water phase for monolayer preparation. Several droplets of the 20–90  $\mu$ L polymer solution were gently deposited so as to disperse evenly on the water surface. The system was left undisturbed for around 30 min until the solvent completely evaporated. Monolayer compression was conducted at 5 mm/min after evaporation to reach the desire surface pressure. The monolayer of the polymer was transferred from the air–water interface by pulling up the silicon substrate vertically at a rate of 2 mm/min.

Growth of Gold Nanoparticles within the Star  $PS_nP2VP_n$ Monolayers. Figure 2 shows the procedure for the fabrication of LB monolayers and the growth of gold nanoparticles from the liquid—solid interface. First, the  $PS_nP2VP_n$  monolayer film was deposited on a silicon substrate and submerged into two different concentrations of HAuCl<sub>4</sub> solution (0.75 or 0.0075 wt %) for 24 h. Consequently, HAuCl<sub>4</sub> formed a complex with the star copolymer monolayer on the solid substrate by protonating pyridine groups in the  $PS_nP2VP_n$  monolayer with H<sup>+</sup> from HAuCl<sub>4</sub> and the remaining AuCl<sub>4</sub><sup>-</sup> binding to the protonated pyridine units. Then, the substrate was washed with Nanopure water to remove



 $PS_nP2VP_n$  heteroarm star copolymer n = number of arms (9 and 28)



**Figure 1.** Schematic of the star  $PS_nP2VP_n$  monolayers. (A) Molecular structure of the  $PS_nP2VP_n$  heteroarm star copolymer. (B) Side view of the molecule at the air-water interface. (C) The air-solid interface as discussed in the text.



**Figure 2.** Growth of gold nanoparticles on the star  $PS_nP2VP_n$  monolayer.

unbound HAuCl<sub>4</sub>, and the sample was submerged in a 0.15 wt % sodium citrate solution for 12 h at 70 °C to synthesize the gold nanoparticles.<sup>54</sup> Sodium citrate will reduce Au ions to  $Au^0$ , which finally aggregate to form gold nanoparticles stabilized by the pyridine groups in the PS<sub>n</sub>P2VP<sub>n</sub> monolayer. Finally, the sample was washed with Nanopure water again to remove excessive sodium citrate and salts.

**Characterization.** The surface morphology of the  $PS_nP2VP_n$ monolayers was characterized by AFM. The AFM images were obtained with a Multimode microscope in light tapping mode according to the usual procedure.<sup>55,56</sup> The thickness of the monolayer was obtained from a scratch test. The height difference between bare silicon and the top of the film was taken to determine the thickness of the film. Also, an M-2000U spectroscopic ellipsometer with WVASE32 analysis software was utilized to confirm the film thickness. TEM was performed on a



**Figure 3.** Surface pressure—area isotherms of PS<sub>9</sub>P2VP<sub>9</sub> and PS<sub>28</sub>P2VP<sub>28</sub> star copolymers.

JEOL 100CX-2 electron microscope and operated at 100 kV to analyze the characteristics of the gold nanoparticles. The samples for TEM have been prepared by using the LB technique on gold grids coated with a carbon support layer. The particle size was calculated from TEM images using ImageJ 1.43u software (National Institutes of Health) by following the regular image analysis procedure.

The UV–visible spectra of the gold star  $PS_nP2VP_n$  hybrid can be obtained by using a UV-2450 spectrophotometer (Shimadzu). The samples for UV–visible measurements have been prepared by depositing LB monolayers on a glass substrate. The monolayer has been submerged in 0.75 wt % HAuCl<sub>4</sub> solution for 24 h, followed by reduction with sodium citrate for 12 h at 70 °C. The submersion and reduction were repeated up to four times to increase the nanoparticle density.

## RESULTS AND DISCUSSION

**Chemical Composition.** Two types of  $PS_nP2VP_n$  heteroarm star copolymers with similar P2VP weight fractions but different numbers of arms and molecular weights were used in this study (Table 1).  $PS_9P2VP_9$  represents a star copolymer with 9 PS and 9 P2VP arms, and  $PS_{28}P2VP_{28}$  represents a star copolymer with a total of 28 arms each. PS domains are hydrophobic, but P2VP chains are relatively hydrophilic because of ionizable pyridine groups that are protonated under acidic conditions ( $pK_a \approx 4.5$ ).<sup>57,58,60,59</sup> The weight percentages of P2VP blocks of both  $PS_9P2VP_9$  and  $PS_{28}P2VP_{28}$  (0.8 and 0.84, respectively) signify that the major fractional component of both star copolymers is the P2VP phase. Although both  $PS_9P2VP_9$  and  $PS_{28}P2VP_{28}$  are similar in chemical composition,  $PS_9P2VP_9$  exhibits remarkably less monomer density and less charge density upon protonation than does  $PS_{28}P2VP_{28}$ because of its lower arm density.

**Surface-Pressure Isotherms.** The pressure—area isotherms of  $PS_nP2VP_n$  heteroarm star copolymers shown in Figure 3 were measured to explore the surface assembly behavior of amphiphilic star copolymers and their ability to complex with the gold precursor as described in detail elsewhere.<sup>60</sup> As known, at the air—water interface, hydrophobic PS forms a collapsed domain on top of the hydrophilic P2VP arms, forming an underlayer in contact with water (Figure 1B).<sup>60,61</sup> At higher surface pressure, the  $PS_nP2VP_n$  heteroarm star copolymers form a dense, uniform monolayer whereas the star polymers have a gaslike phase at low surface pressure (nominally no compression). After transferring to a silicon substrate, the P2VP arms spread in the bottom part and form an intimate contact with the hydrophilic substrate and



**Figure 4.** High-resolution AFM images (height, left; phase, right) of the star  $PS_nP2VP_n$  monolayer at a surface pressure of 0 mN/m:  $PS_9P2VP_9$  (A) before and (B) after gold nanoparticle synthesis.  $PS_{28}P2VP_{28}$  (C) before and (D) after gold nanoparticle synthesis. The scale bar is 100 nm for all images. The *z* scale is (A, C) 10 nm for images before the synthesis and (B, D) 40 nm for images after the synthesis.

the PS-phase aggregates in the center of the micelle (Figure 1C) as will be discussed later.

Adding HAuCl<sub>4</sub> to the subphase resulted in the formation of uniform complexation between HAuCl<sub>4</sub> in the subphase and  $PS_nP2VP_n$  heteroarm star copolymers at the air—water surface because of the higher affinity of the pyridine functional group for the gold ion via electrostatic interaction. Notably, the isotherm in Figure 3 shows the change in molecular area for both PS<sub>9</sub>P2VP<sub>9</sub> and PS<sub>28</sub>P2VP<sub>28</sub> after adding 0.0001 M HAuCl<sub>4</sub> to the LB trough. The increase in the molecular area of the monolayer film on the water interfaces of both PS<sub>9</sub>P2VP<sub>9</sub> and PS<sub>28</sub>P2VP<sub>28</sub> indicates the ion adsorption of polar P2VP domains.<sup>62,63</sup> The change in the molecular area of PS<sub>9</sub>P2VP<sub>9</sub> because of the greater number of amine groups and hence the

greater capacity to bind Au ions that can be ascribed to the high chain density of multiarm star architecture (Table 1). The highly compact structure of the star polymer is known to affect ionization and condensation with a counterion as well as with the osmotic pressure inside macromolecules. As shown for PS<sub>9</sub>P2VP<sub>9</sub> heteroarm star copolymers, the surface pressure reached 50 mN/m after a forming complex with Au ions. This increased monolayer stability suggests the change in chain conformation at higher surface pressure resulting from the interaction between Au ions and P2VP arms. Similarly, the PS<sub>28</sub>P2VP<sub>28</sub> heteroarm star copolymers were also found to undergo a pronounced phase transition at a higher surface pressure from 20 to 35 mN/m, indicating the variation in chain conformation influenced by gold ions.<sup>38,64</sup>

**Surface Morphologies.** To investigate the growth of nanoparticles and the stability of the LB monolayer, we examined the variation in surface morphology before and after the reduction of gold nanoparticles. In this study, we focus on gold nanoparticle synthesis at the liquid—solid interface with ionizable pyridine containing  $PS_nP2VP_n$  heteroarm star copolymers as a template allowing for the stabilization of gold ions on a silicon substrate. We expose the  $PS_nP2VP_n$  monolayer transferred from the air—water interface to  $HAuCl_4$  solution at pH 1.0 to enable the binding of  $AuCl_4^-$  with the protonated  $PS_nP2VP_n$  monolayer and subsequently reduce  $AuCl_4^-$  with sodium citrate to promote the formation of gold nanoparticles.

The surface morphologies of the LB monolayers of  $PS_9P2VP_9$ and  $PS_{28}P2VP_{28}$  heteroarm star copolymers at the lowest surface pressure (nominally 0 mN/m) are shown in Figure 4. (See Supporting Information, Figure S1 for large-area scans.) The AFM images (both topography and phase) show individual dots representing star copolymer micelles in the gaslike phase at the lowest surface pressure for a low concentration of polymer solution. For PS<sub>9</sub>P2VP<sub>9</sub>, the size of individual P2VP domains on the silicon substrate is about 1.5 nm in height and 20 nm in the lateral dimension. P2VP aggregates of  $PS_{28}P2VP_{28}$  are larger than those of  $PS_9P2VP_9$  because of the greater number of arms and the total molecular weight (Table 1). From Figure 4C, the average P2VP domain in the copolymer is around 4.5 nm in height and 39 nm in dimension, which corresponds well to previous reports.<sup>43,65</sup>

To explore the effect of the change in surface aggregation on the growth of gold nanoparticles, we compared the surface morphology at different surface pressures (0 and 10 mN/m). At 0 mN/m, the surface morphology of the original monolayers was changed dramatically after exposure to gold salt. PS<sub>9</sub>P2VP<sub>9</sub> block copolymers with gold nanoparticles possess several layers of nanoparticles (Figures 4B). In contrast, the PS<sub>28</sub>P2VP<sub>28</sub> monolayer contains individual nanoparticles after gold reduction (Figures 4D). The  $PS_nP2VP_n$  heteroarm star copolymers, both PS9P2VP9 and PS28P2VP28, are swelled after exposure to  $HAuCl_4$  because of the electrostatic repulsion from the proto-nated P2VP arms.<sup>43,46,66</sup> After reduction with sodium citrate, gold nanoparticles are formed inside the  $PS_nP2VP_n$  monolayer and retain their swelled structure. For PS<sub>9</sub>P2VP<sub>9</sub>, it is possible those P2VP domains may swell and partially overlap because of the close distance between neighboring micelles. In contrast to PS<sub>9</sub>P2VP<sub>9</sub>, the surface morphology of PS<sub>28</sub>P2VP<sub>28</sub> still shows individual dots on the silicon substrate both before and after gold reduction. Figure 4C indicates that the distance between each PS<sub>28</sub>P2VP<sub>28</sub> micelles is greater than the size of PS<sub>28</sub>P2VP<sub>28</sub> micelles, which prevents the partial overlap of P2VP chains from



**Figure 5.** TEM images (A, B) and corresponding histogram (C, D) of gold nanoparticles grown on  $PS_nP2VP_n$  heteroarm star copolymers at surface pressure 0 mN/m and gold solution concrentration, [HAuCl<sub>4</sub>] = 0.75 wt %: (A), (C) PS<sub>9</sub>P2VP<sub>9</sub> and (B), (D) PS<sub>28</sub>P2VP<sub>28</sub>.

Table 2. Thickness of the  $PS_nP2VP_n$  Composite Film and Size of the Gold Nanoparticles

			film thic						
composition	surface pressure (mN/m)	[HAuCl <sub>4</sub> ] %	star monolayer	gold-star polymer composite	particle size (nm) <sup>b</sup>				
PS <sub>9</sub> P2VP <sub>9</sub>	10	0.75	$1.6\pm0.28$	$6.3\pm0.45$	$7.1\pm1.9$				
	0	0.75	$1.0\pm0.18$	$7.2\pm1.17$	$6.0\pm2.8$				
$\mathrm{PS}_{28}\mathrm{P2VP}_{28}$	10	0.75	$2.0\pm0.37$	$24.6\pm5.49$	$6.5\pm1.7$				
	10	0.0075	$2.0\pm0.31$	$7.3\pm0.87$	$7.0\pm1.8$				
	0	0.75	$3.1\pm0.35$	$10.9 \pm 1.53$	$4.9\pm2.2$				
<sup><i>a</i></sup> Measured from a scratched film by AFM. <sup><i>b</i></sup> Measured by TEM.									

the swelled neighboring micelles. As a result,  $PS_{28}P2VP_{28}$  retained separate micelles even after gold reduction.

AFM images do not reflect the actual dimension of gold nanoparticle because the height measured includes contribution from the star polymer templates (Figure 12C). Thus, the shape and size of the gold nanoparticles were independently determined by TEM. Aggregation of the nanoparticles seen in some areas can be due to the swelling effect of the  $PS_nP2VP_n$  LB film and partial dewetting of hydrophilic-hydrophobic monolayers after transfer to a hydrophobic carbon support. However, to reduce the error in the particle size measurement due to the present of aggregates, we utilized ImageJ program to analyze the gold nanoparticle size and selected only individual dots to calculate the gold nanoparticle size because the overlap structures prevent the observation of actual perimeter of the nanoparticles. The number of individual nanoparticles in each TEM images is more than 50 units and is sufficient to calculate the particle size reliably. The analysis result was reproducible and was consistent over the different areas. Figure 5 shows TEM images of star PS<sub>n</sub>P2VP<sub>n</sub>/gold nanoparticles monolayer at the lowest surface pressure along with histograms of size distribution



**Figure 6.** High-resolution AFM images (height, left; phase, right) of the star  $PS_nP2VP_n$  monolayer at a surface pressure of 10 mN/m:  $PS_9P2VP_9$  (A) before and (B) after gold nanoparticle synthesis.  $PS_{28}P2VP_{28}$  (C) before and (D) after gold nanoparticle synthesis. The scale bar is 100 nm for all images. The *z* scale is (A, C) 10 nm for images before the synthesis and (B, D) 50 nm for images after the synthesis.

calculated from these images. As clear from these images, gold nanoparticles are spherical with the average particle size somewhat similar for both star block copolymers: 6.0 and 4.9 nm for  $PS_9P2VP_9$  and  $PS_{28}P2VP_{28}$ , respectively (Table 2). The histograms show that  $PS_9P2VP_9$  monolayer possesses a broader size distribution of gold nanoparticles, which imply the less stringent confined conditions for nanoparticle formation. Indeed, the  $PS_9P2VP_9$  monolayer contains lower ratio P2VP phase to gold ion, which stabilizes gold nanoparticles, than  $PS_{28}P2VP_{28}$  monolayer. Higher concentration of amine groups is critical for the prevention of agglomeration and growth of smaller nanoparticles.<sup>67</sup>

Figure 6 (large-area scans in Supporting Information, Figure S2 for large area scans) presents AFM images of PS<sub>9</sub>P2VP<sub>9</sub> and PS<sub>28</sub>P2VP<sub>28</sub> on silicon substrates at a higher surface pressure of



**Figure 7.** TEM images and a corresponding histogram of gold nanoparticles formed from  $PS_nP2VP_n$  heteroarm star block copolymers at a surface pressure 10 mN/m and a gold solution concentration of [HAuCl<sub>4</sub>] = 0.75 wt %: (A, C) PS<sub>9</sub>P2VP<sub>9</sub> and (B, D) PS<sub>28</sub>P2VP<sub>28</sub>.

10 mN/m. At this pressure, both star block copolymers form a dense monolayer at the air—water interface under these conditions with densely packed micelles. AFM images in Figure 6A,C show the uniform morphology of the transferred star copolymer from the air—water interface. The uniformity of this structure on exposing the polymer film to HAuCl<sub>4</sub> solution and on further reduction with sodium citrate is significantly affected by swelling effects. Also, the LB monolayer composed of interconnected P2VP chains may have uneven gold ion absorption on the P2VP layer, leading to partial aggregation and a broad size distribution of gold nanoparticles.

The AFM and TEM images are different because the AFM images display the spherical micellar structure of  $PS_nP2VP_n$ heteroarm star copolymers encompassing the gold nanoparticles whereas the TEM images exhibit only gold nanoparticles in the LB film. However, both AFM and TEM images demonstrate a trend in the gold nanoparticle distribution. At the lowest surface pressure after gold reduction, the  $PS_nP2VP_n$  monolayer exhibits partially aggregated and swelled micelles after gold reduction as shown in the AFM images (Figure 4B), which thereby likely lead to unevenly distributed gold nanoparticle as shown in the TEM image (Figure 5A). This result can be attributed to the insufficient stabilization of gold nanoparticle by P2VP star copolymer micelles. At high surface pressure, the monolayer exhibits denser micelle organization with a more uniform distribution (AFM in Figure 6), which is compatible with highly dense nanoparticle morphology as demonstrated in the TEM image (Figure 7).

The thickness of the polymer film before and after gold reduction provides further information for understanding the formation behavior of gold nanoparticles within the polymer film. Figure 6A,C confirms the uniformity of the polymer film on the silicon substrate. The thickness of the  $PS_nP2VP_n$  monolayer film in Table 2 is measured using AFM with a scratch test of the polymer deposited on the silicon substrates (not from TEM samples). The film thickness was measured from more than three different areas in large-area AFM scans (20  $\mu$ m size). As shown, the standard deviation values tend to increase with increasing film thickness, and the standard deviation is within 20%. Moreover, AFM thickness measurements were independently confirmed with ellipsometry when possible.



**Figure 8.** AFM images (height, left; phase, right) of gold nanoparticle/ PS<sub>28</sub>P2VP<sub>28</sub> heteroarm star copolymers at a surface pressure of 10 mN/m and a gold solution concentration of  $[HAuCl_4] = 0.0075$  wt %. The scale bars are (A) 200 and (B) 100 nm. The *z* scale is 10 nm for both A and B.

At a high surface pressure, the film thicknesses of PS<sub>9</sub>P2VP<sub>9</sub> and PS<sub>28</sub>P2VP<sub>28</sub> films before gold incorporation are around 1.6 and 3.1 nm, respectively, which are much higher than that for the  $PS_nP2VP_n$  monolayer at the lowest surface pressure (Table 2). The film thickness from AFM scratch tests is in good agreement with that obtained by ellipsometer (Table 2). The film thickness of the PS<sub>9</sub>P2VP<sub>9</sub> monolayer increases to 6 nm after gold nanoparticle formation. This indicates the formation of the individual gold nanoparticles in the PS<sub>9</sub>P2VP<sub>9</sub> ultrathin film. In contrast to PS<sub>9</sub>P2VP<sub>9</sub>, the thickness of PS<sub>28</sub>P2VP<sub>28</sub> increases dramatically from 2 to 25 nm after gold nanoparticle formation (Table 2). Such a thickness increase is observed even though the size of the gold nanoparticles in the PS<sub>28</sub>P2VP<sub>28</sub> monolayer is only 6.5 nm. This difference suggests that the gold nanoparticles form multilayer aggregates within the monolayer of  $PS_{28}P2VP_{28}$ . This high concentration of nanoparticles formed is due to the high concentration of pyridine groups available for gold reduction in the continuous P2VP phase. Moreover, the size distribution of gold nanoparticles for densely packed star block copolymers (at 10 mN/m) becomes more narrow (Table 2).

As a next step, we applied HAuCl<sub>4</sub> at two different concentrations, 0.75 and 0.0075 wt %, to compare the effect of the gold ion concentration on nanoparticle formation. The AFM images in Figure 8 indicate that the gold nanoparticles formed at 0.0075 wt % HAuCl<sub>4</sub> form a monolayer whereas larger aggregates of gold nanoparticles are formed at a 0.75 wt % HAuCl<sub>4</sub> concentration. At 0.0075 wt % HAuCl<sub>4</sub>, a much higher ratio of the P2VP group is available to stabilize the gold nanoparticles and facilitate a narrow size distribution. The TEM image in Figure 9 clearly shows a much lower gold nanoparticle density compared to that of 0.75 wt % HAuCl<sub>4</sub> because of the smaller number of gold ions available for reduction. The diluted HAuCl<sub>4</sub> solution provides fewer AuCl<sub>4</sub> ions to bind with PS28P2VP28 and causes a low density of gold nanoparticles within the star copolymer template. In contrast to diluted HAuCl<sub>4</sub>, 0.75 wt % HAuCl<sub>4</sub> has a larger number of gold ions with which to grow high-density nanoparticles, thus affecting



**Figure 9.** (Left) TEM image and (right) corresponding histogram of gold nanoparticles with  $PS_{28}P2VP_{28}$  heteroarm star copolymers at a surface pressure 10 mN/m and a gold solution concentration of  $[HAuCl_4] = 0.0075$  wt %.



**Figure 10.** UV—vis absorption spectra of gold nanoparticles grown on the star  $PS_{28}P2VP_{28}$  monolayer with four different repeating cycles of the gold reduction.

their layering in  $PS_{28}P2VP_{28}$ . Finally, it is worth noting that adding 0.0001 M HAuCl<sub>4</sub> to the subphase does not significantly affect the surface morphology and dimensions of the gold nanoparticles formed (isotherms in Figure 3, data not shown).

Independent confirmation of the gold nanoparticle formation and information on their aggregation status can be obtained from the UV-vis spectra of gold nanoparticles grown in star copolymer templates (Figure 10). The samples for UV-vis measurement are prepared by the deposition of star PS28P2VP28 copolymers on a clean glass substrate at a surface pressure of 10 mN/m. The gold reduction procedure was repeated several times to increase the density of gold nanoparticles. After the gold reduction procedure was repeated, an absorption band at 530 nm appeared that corresponds to a gold nanoparticle plasmon band.<sup>68-70</sup> The peak position agrees with the formation of 3-7 nm gold nanoparticles known in the literature and thus confirms our TEM observations.<sup>20,30</sup> The absorption bands are located at the same position irrespective of the number of times the reduction was repeated, and the absorption intensity increased with the corresponding increase in nanoparticle density. The constant peak position indicates uniformity in the size of gold nanoparticles without larger aggregates.

A summary of all monolayer thickness variations under different fabrication conditions is presented in Figure 11. As apparent from the results discussed above, the P2VP chains conformation and the state of the microphase separation play



**Figure 11.** Thickness of the star  $PS_nP2VP_n$  monolayer film before and after reduction at surface pressures of 0 mN/m (SP0) and 10 mN/m (SP10).



**Figure 12.** Schematic representation of the growth of gold nanoparticles in  $PS_nP2VP_n$  heteroarm star block copolymers. Star  $PS_nP2VP_n$  monolayer at the air—silicon interface (A) before exposure, (B) after exposure to the gold solution (AuCl<sub>4</sub><sup>-</sup>), and (C) after gold reduction by sodium citrate.

very important roles in controlling the gold nanoparticle size distribution. For our systems, P2VP domains form an underlying layer to interact with hydrophilic surfaces such as the water subphase and silicon substrate (Figure 12A). The  $AuCl_4^-$  ions are bound to the underlying P2VP layer with protonated pyridine units on the silicon substrate.<sup>54,71</sup> The particle size distribution depends on the number of P2VP units and the gold ion concentration, but the nanoparticles dimensions always stay with

5-7 nm, which could be attributed to the confinement of the P2VP domain structure of the star polymer considering the film thickness (Figure 12B,C). Such distinct micellar stability and suppression of nanoparticle aggregation common in solution-based reduction are likely due to the dense chain state in multiarm star architecture in contrast to that in conventional micelles composed of linear block copolymers.

## CONCLUSIONS

We demonstrated the in situ synthesis of individual gold nanoparticles on monolayers of  $PS_nP2VP_n$  star copolymers at the liquid—solid interface. In this study, electrostatic interactions were utilized to incorporate  $AuCl_4^-$  into the protonated P2VP chains, which form a continuous film underneath the PS aggregate to interact with the hydrophilic substrate. We demonstrated that the LB monolayer composed of star copolymer surface micelles can act as a template for nanoparticle growth in the one-sided P2VP microphase. The gold nanoparticle growth can be controlled by the surface pressure, HAuCl<sub>4</sub> concentration, domain morphology, and number of P2VP arms. UV—vis spectra and TEM images confirm the formation of the gold nanoparticles with an average size of  $6 \pm 1$  nm.

# ASSOCIATED CONTENT

**Supporting Information.** AFM images of the star  $PS_nP2VP_n$  monolayer. This material is available free of charge via the Internet at http://pubs.acs.org.

## AUTHOR INFORMATION

Corresponding Author

\*E-mail: vladimir@mse.gatech.edu.

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