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Gold nanoparticles adsorption study onto periodic block copolymer using quartz crystal microbalance

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ABSTRACT

In this work, we have studied adsorption and aggregation characteristics of citrate stabilized gold nanoparticles (AuNPs) onto periodic block copolymer using a quartz crystal microbalance (QCM) technique. Thin film of polystyrene block-poly (2-vinylpyridine) (PS-b-P2VP) template was coated onto gold Q-sense sensor crystals to study the adsorption and aggregation characteristics of AuNPs. The template pattern was controlled through an oxygen plasma reactive ion etching (RIE) process. Height of the template was varied from 50 nm to 20 nm with the inter-particle separation of ~200 nm. Adsorption studies of AuNPs were carried out in-situ and in real time by means of the QCM technique. There is change in frequency of the Q-sense sensor crystal with the variation in mass/volume of pattern polymer template. The adsorption and aggregation characteristics of AuNPs onto a pattern template substrate were studied using AFM and QCM analysis. The arrays of gold nanoparticle clusters presenting a systematic variation in number of AuNPs due to different template dimensions show a mean intra-particle separation below 10 nm.

1. Introduction

Metal nanoparticles are of significant interest in the field of materials science, primarily due to their optical and electronic properties [1]. Among several metal nanoparticles, AuNPs exhibit promising characteristics and have found applications in catalysis and biology [2], memory devices [3,4] and sensing [5,6]. AuNPs have been broadly used in sensor technology, particularly as a transducer platform for the fabrication of biosensors [7]. The AuNP-composites have also been used for glucose sensor and chemical sensor applications [8–9]. The concentration of AuNPs has been reported in the QCM delicate film as a factor of AuNPs adsorption [10]. QCM technique has also been used in real time to monitor the bio-molecular interaction [11], thin film deposition rate, detergency process [12], and adsorption of nanoparticles [13]. The frequency change of a quartz crystal resonator was proportional to the added mass ($\Delta m = -C \times \Delta f$) [14]. This resonance frequency relies on the mass, thickness, shape and chemical structure of the crystal wafer, and physical properties of the surrounding media [14–15]. In order to improve the sensitivity of the crystal and at the same time maintain mechanical property, it is essential to increase the surface area of the crystal by coating a thin film layer of polyelectrolyte material on the crystal surface [13].

Adsorption and aggregation characteristics of AuNPs can be varied through the template-surface morphology, particle size, and packing of the particles. Generally, periodic block copolymer thin films are suitable candidate for the assembly of nanoparticles in a different texture [16–17]. Here, we report the adsorption and aggregation characteristics of AuNPs onto a PS-b-P2VP block copolymer patterned template with different height of the polymer. The adsorption kinetic was monitored in real time through QCM analysis and ex-situ AFM analysis. Change in mass–frequency of the sensor was observed with respect to polymeric template height. QCM and AFM analyses reveal that the adsorption and aggregation of AuNPs in a closed-packed structure varied through the control of polymer template height. Furthermore, such patterned templates can be used for the detection of negatively charged biomolecules.

2. Experimental

Materials: PS-b-PVP (molecular weight: 248,000-b-195,000; g/mol) was purchased from Polymer Source Inc. (Montreal, Canada). Hydrogen tetrachloroaurate (III) trihydrate ($HAuCl_4 \cdot 3H_2O$) (99.9%) and sodium citrate dihydrate (99%) were purchased from Aldrich.

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4.95 MHz ± 50 kHz AT-cut gold sensor crystals with an active sensor area of 14 mm^2 were purchased from Q-Sense (Sweden).

Experimental details: Thin films of 443 kDa PS-b-P2VP reverse micelles were coated from m-xylene solutions at polymer concentration of 0.5% *w*/*w* on to QCM substrates by spin-coat at a speed of 8000 rpm with relative humidity of 60%. RIE was performed to get a different height of the template, wherein the heights of the micelles were controlled by O_2 plasma RIE (oxford plasma lab100, Oxford instruments, UK) for duration of 0 s, 20 s, and 70 s at 30 W. The working pressure and O_2 gas flow rate during plasma treatment were 65 mTorr and 20 sccm, respectively. The polymer coated gold Q-sense sensor crystals were employed in the flow-type measurement Q-Sense QCM-D (D300) chamber at room temperature. When the frequency signal reached a stable level in DI water at 25 °C, 2 mL of citrate-stabilized AuNPs suspension (pH 5.8) was injected. Typically, 80 μL of the colloidal solution retain on the crystal surface. AuNPs were prepared by a citrate reduction method as reported earlier [18,19]. The synthesized AuNPs are spherical in shape with diameter of ~11 nm [19].

For QCM study, frequency and voltage changes were examined throughout the process until the frequency reached a new stable level in DI water. The frequency difference for 5 MHz of Q-sense crystal between the two stable signals before and after injection of AuNPs was taken as ΔF. Samples were rinsed out with DI water for surface characterization using atomic force microscope (AFM) in tapping mode (Nano scope IV Multimode AFM, Veeco Instruments Inc., NY, USA).

3. Results and discussion

Fig. 1 shows AFM images for different heights of the polymer micelles onto the gold Q-sense sensor crystals. The height of PS-b-P2VP reverse micelles is 50 nm without etching and was systematically varied to 43 nm and 20 nm by O_2 plasma RIE for 20 s and 70 s durations, respectively. The pattern polymer template having inter-particle separation of 200 nm was obtained. Fig. 1 also shows the uniformity of periodic block copolymer coated gold Q-sense sensor crystals. From AFM analysis, it was found that the etching rate of block copolymer is 0.35 nm/s.

To study the AuNPs adsorption and aggregation characteristics, AFM characterization was carried out after the QCM experiment. Formation of AuNPs cluster onto the micelles was observed (Fig. 2). The AuNPs cluster formation is due to the electrostatic interaction between AuNPs and PS-b-P2VP copolymer with mean intra-particle separation of < 10 nm. The density of AuNPs onto PS-b-P2VP reverse micelles was varied systematically with the template height. The AuNPs density decreases with decrease in the height of the micelles. The adsorption characteristics of AuNPs were observed for the template heights of 50 nm and 43 nm. The presence of AuNPs aggregation onto the

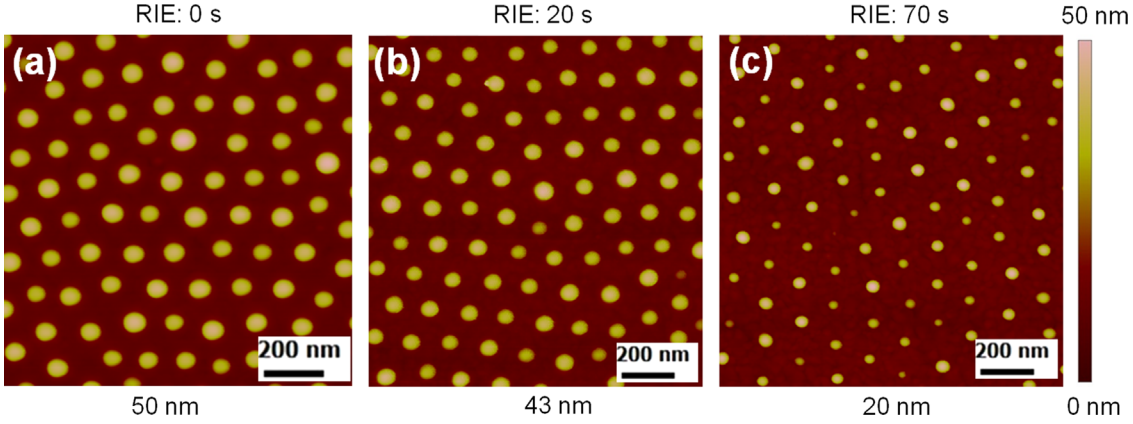

Fig. 1. Tapping mode AFM images of PS-b-P2VP with respect to different height of the polymer. Different polymer height was obtained through the etching of polymer using oxygen plasma in RIE system. The polymer was etched for (a) 0 s (corresponds to polymer height of 50 nm), (b) 20 s (corresponds to polymer height of 43 nm), and (c) 70 s (corresponds to polymer height of 20 nm).

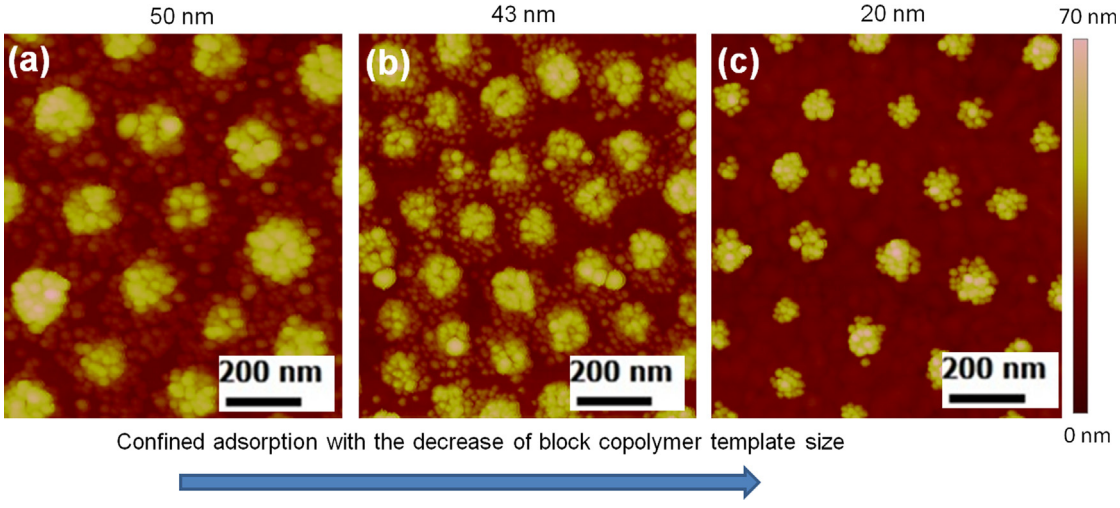

Fig. 2. Tapping mode AFM images of AuNPs clusters with respect to different height of the polymer after in-situ QCM experiment. (a) Polymer height of 50 nm, (b) polymer height of 43 nm, and (c) polymer height of 20 nm.