Localized surface plasmon resonance (LSPR) sensitivity of Au nanodot patterns to probe solvation effects in polyelectrolyte brushes†‡

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We report localized surface plasmon resonance (LSPR) of hexagonal Au nanodot arrays to detect changes in the thickness and conformation of poly[2-(methacryloyloxy)ethyltrimethyl ammonium chloride] (PMETAC) brushes.

Recently, metallic nanoparticles and nanostructures have been successfully employed as molecular-recognition elements and amplifiers in biosensors, using evanescent electromagnetic fields such as propagating surface plasmon resonance (SPR).[1] The plasmon induced enhancement of the electromagnetic field near the metal surface has been used extensively in sensors, and more recently also to amplify fluorescence and Raman scattering.[2] In sensor applications, the changes in the plasmonic resonance wavelength of maximum absorption or scattering are monitored as a function of changes in the chemical and physical environment of the surface of the nanoparticles. Here, a high sensitivity of the spectral response of the plasmonic resonance absorption band to changes in the refractive index of the surroundings is desired to detect molecules. From the viewpoint of sensitivity, unique metal structures have been at the centre of attention.[3] Many theoretical and experimental studies have been made on metal nanopatterns with different geometries to find the best configuration to enhance the sensitivity of the plasmon resonance.[4] Most importantly, precise spatial positioning of the nanostructures, without any specific capping agents or stabilizers, accounts for the sensitive detection of changes in the physicochemical properties of the surface. The wavelength corresponding to the extinction maximum of the LSPR (λ_{max}) is strongly dependent on the dielectric properties of the medium. Tokareva et al. exploited this sensitivity in the study of the pH-induced swelling of polyelectrolyte brushes adsorbed onto gold nanoislands.[5] These results indicate that the sensitivity of the plasmon response of Au nanodot pattern arrays can be used as analytical tools to study polymer brush growth.

In this study, we examine the characteristic behavior of the LSPR spectra of patterned arrays of Au nanodots of various thicknesses which were fabricated by colloidal lithography. These nanodots were sandwiched between two glass slides and cationic brushes of [2-(methacryloyloxy)ethyl]trimethyl-ammonium chloride (METAC), with well-known actuating or switching properties in electrolyte solution,[6] were grown from the 20–60 nm high cylindrical surfaces only (as shown in Fig. 1). Despite the extremely small amount of polymer in this system, we were able to analyze the thickness and conformational changes of PMETAC brushes by following λ_{max}, opening up routes to characterize responsive surfaces without conventional characterization systems such as ellipsometry or atomic force microscopy (AFM).[7] It is known that both the diameter and the center to center distance of metal nanodots have a significant influence on the peak position and shape of the LSPR signal.[8] Similarly, by varying the dot thickness, significant changes in the position and intensity of the peak were obtained. In this case, samples of disk shapes of similar diameter ($\sim$100 nm) and period ($\sim$220 nm) but with three different thicknesses: 20 (T1), 40 (T2) and 60 nm (T3), were analyzed. (Refer to S1, ESI for details†) As can be seen in Fig. 2(A), the extinction wavelength was blue shifted from λ_{max} = 670 nm to 580 nm as the pattern thickness increased from 20 nm to 60 nm.

In order to elucidate the peak shift observed in the experiments, the discrete dipole approximation (DDA) method was used to theoretically model the optical response of the patterns.[9] The

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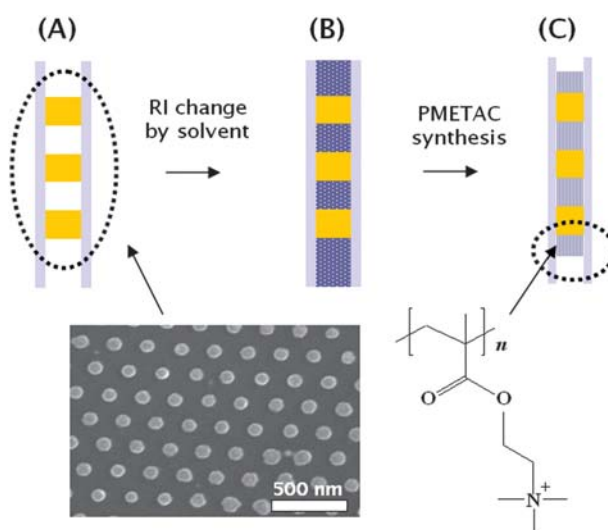
Fig. 1 Representative SEM image of the hexagonal dot array with $D \approx$ 100 nm and 220 nm periods which used the substrate for sensing of the polymer brush (A). Experimental scheme for LSPR modulation of Au arrays in different refractive index media (B) and with surface modification by PMETAC (C).
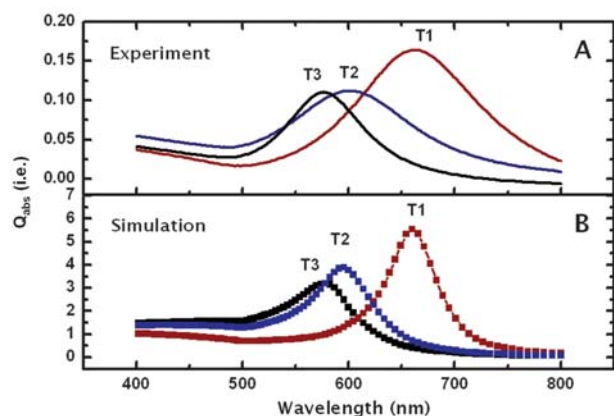
Fig. 2 Experimental (A) and calculated (B) absorption spectra of bare Au nanodot arrays with different thicknesses; T1 (20 nm), T2 (40 nm), and T3 (60 nm).

calculation has been carried out under an assumption that the nanodots are cylindrical disks. The dipole grid spacing and the diameter of the cylindrical disk is 2 nm and 100 nm, respectively. Fig. 2(B) shows the calculated efficiency factors for optical absorption of the patterns with different Au thicknesses as in the experiments (T1 to T3). The calculated widths are smaller than the measured ones, which indicates some polydispersity in the Au nanopatterns on the surface, resulting from distortions in the PS colloidal particle array. However, it clearly shows that the experiment and calculation agree well in terms of the peak positions. The blue-shift of the peak position with increasing the Au nanodot thickness is consistent with previous studies.[10]

For the application of metal nanopatterns as bio or chemical sensors, it is important to understand the dependence of the LSPR wavelength of metal nanopatterns on the refractive index of the surrounding medium. To do this, we observed the LSPR peak change when the surrounding media were replaced with solvents having a range of different refractive indices. For convenience and a better control over the extinction measurements we fabricated a sandwich structure with the nanopatterns encapsulated between two glass slides and introduced the solvents between pattern and cover glass as shown in Fig. 1(B). LSPR sensitivities of the three samples were determined by comparing the shift in λ_{max} to the change in the refractive index of the surrounding medium. Fig. 3 shows a plot of λ_{max} vs. refractive index. For the patterns with 40 and 60 nm thick Au, we see a linear and very similar dependence of $\Delta\lambda_{max}$ on the surrounding refractive index as expected, but there are significant deviations for the thin Au dots. From Fig. 3 we can also calculate the sensitivity factor S ($\Delta\lambda_{max}$/RIU) which is defined as the relative changes in resonance wavelength with respect to a change in the refractive index of the surrounding medium. (See S2, ESI for detail procedure and absorption spectra†) The S of sample according to thickness was calculated as 156 nm/RIU (T1), 71 nm/RIU (T2) and 50 nm/RIU (T3) from the slope of this plot, respectively. The analysis presented in Fig. 3 provides a convenient way of comparing and characterizing the response from the different nanostructures and shows that their sensitivity is affected by geometrical factors, in this case the thickness. The linear relationship between absorption spectra vs. medium refractive index could be modeled by using an extension of Mie's theory
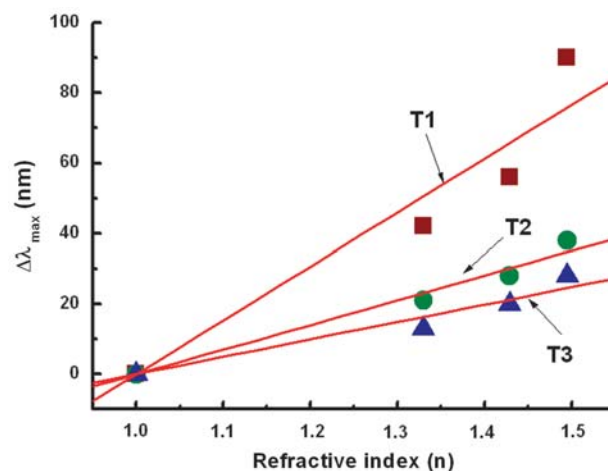

Fig. 3 LSPR sensitivity in response to the dielectric environment. The linear dependence of the LSPR peak shift of Au nanodot arrays of T1, T2 and T3 upon a change in dielectric medium from 1 to 1.5.

in the quasi-static regime within the dipole approximation.[11] Also, the apparently higher sensitivity for thinner metal films is consistent with a recent report by Dahlin et al. which shows smaller peak shifts with deeper holes in the inverted nanopore structure.[12] The intensity of excited surface plasmon modes on Au decays exponentially over a distance of approximately 50 nm. Any shift in the λ_{max} of the LSPR is therefore dominated by the dielectric constant of materials that are physi- or chemisorbed to the surface very closely. We have exploited this surface-selectivity to probe both the thickness of polymer brush layers in air, and the collapse of brushes in high ionic strength solutions. Brushes were grown in a two-step procedure from initiator-modified Au nanopatterns following a previously reported procedure. (See S3, ESI for details†)[6b] Fig. 4(A) shows the thickness as measured by ellipsometry of PMETAC brushes on reference, planar and non-patterned Au substrates and the shift in the LSPR peak ($\Delta\lambda_{max}$) before and after polymerization for various times. It should be noted that the 'dry' thickness of 13.5 nm most likely represents brushes that still contain a significant amount of water, as these polymers are extremely hygroscopic. There is a strong correlation between the thickness of the brushes and $\Delta\lambda_{max}$. Both T1 and T2 samples gave a good linear response to the increase in thickness of the polymer brushes, with the thin gold films (T1) more sensitive than T2 films, consistent with the sensitivity test of a bare Au sample as shown in Fig. 3. Subsequently, the dry polymer brushes were placed in an aqueous environment. Fig. 4(B) and 4(C) show the absorption peaks for T1 and T2, respectively. The black lines show the bare Au samples in water, and the blue traces show the PMETAC brushes in water. Clearly the shift is very small, and even the T1 samples only register a very small change in λ_{max}. In pure water, the PMETAC brushes are swollen and these data indicate that the volume fraction of polymer in these swollen brushes is very low, therefore leading to a refractive index near the surface that is similar to water. The addition of 1N NaCl (red traces, Fig. 4(B) and 4(C)) leads to a collapsed state of the polymer brushes due to screening of the repulsive interactions between the charges on the polymer chains. However, the changes in λ_{max} for the swollen and collapsed states are minimal, indicating that the collapsed state still contains significant fractions of
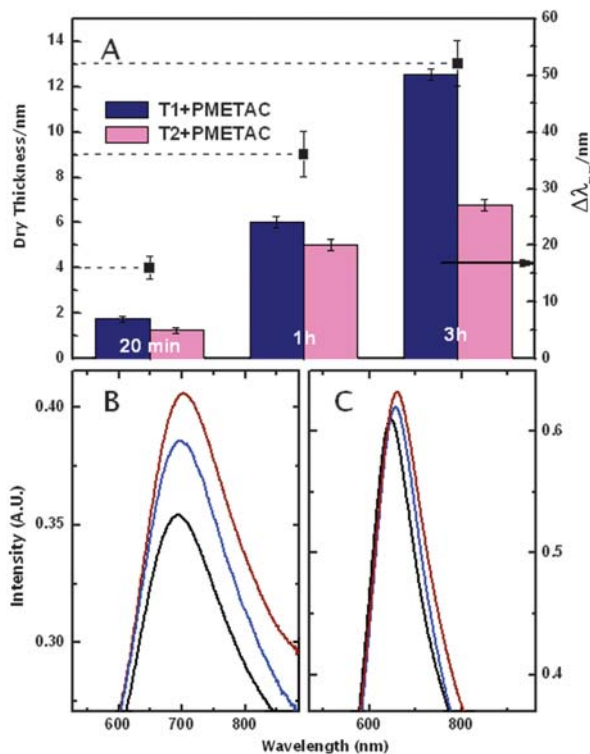
Fig. 4 Ellipsometric thickness of PMETAC polymerized on an Au thin film and the λ of Au samples after polymerization for 20 min, 1 h and 3 h (A). The absorption peaks of samples of T1 (B) and T2 (C) red shifted with respect to bare Au sample in water (black), with the Au sample modified by PMETAC in pure water (blue), and in NaCl (1N) solution (red), respectively.

Fig. 5 λ_{max} value of T1 sample in the different salt solutions. The λ_{max} value of the T1 sample is most red-shifted in the LiClO$_4$ 1N solution because the PMETAC brush is hydrophobically collapsed by the ClO$_4^-$ anions, which are poorly hydrated.

water. From previous studies, we know that the nature of the counterion can have a dramatic impact on the hydration of the brushes.[6b,13] We therefore repeated the collapse studies with different salts. As can be seen in Fig. 5, the value of λ_{max} is clearly influenced by the nature of the counterion.

Fig. 5 shows the changes in λ_{max} for the T1 subsrates. There is a clear contrast between the ClO$_4^-$ and Cl$^-$ anions, with a much stronger red-shift for the former. ClO$_4^-$ anions form ion pairs with the quaternary ammonium groups on the brushes, leading to a 'hydrophobic' collapse[6b] and as a result, the refractive index of these brushes shows a much larger change upon collapse, as there is much less water present in these films.[14] Interestingly, the LSPR signal is also sensitive to the concentration of the salt concentration used. This might point to different states of collapse for the low and high concentrations, although a change in the refractive index due to the increased concentration of ions in the brushes might make a small contribution.

In conclusion, we have demonstrated the use of LSPR on Au nanodot arrays as a tool to probe the hydration in polyelectrolyte brushes. The sensitivity of the LSPR response to changes in the refractive index of the surrounding medium can be increased by varying the thickness of the Au nanodots. The extinction wavelength of the sample blue shifted as the thickness increased, which provides an additional tool for future experiments where we want to study the interaction between the LSPR and dyes covalently attached to the end of the polymer brushes. The shift in the LSPR peak allowed monitoring of the thickness of surface-initiated
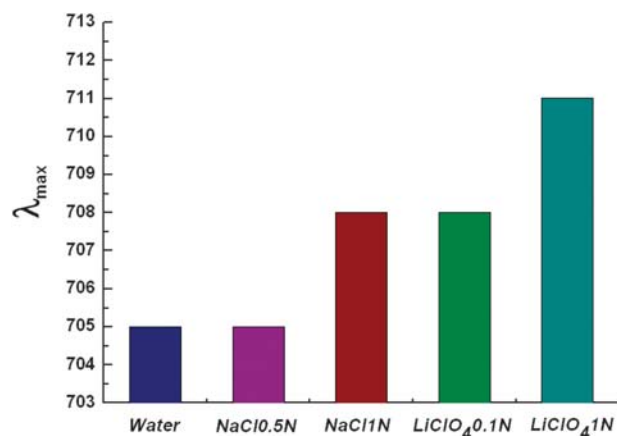
PMETAC brushes and the collapse of the brushes in salt solution could be observed. These sensitive optical elements will provide a valuable tool in the study of polymer brushes, where changes in the hydration of the polymer films form a key part of future sensor designs.

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