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Binary Nanoparticle Assemblies for Generating Chemical Patterns

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INTRODUCTION: Many approaches have focused on preventing protein adsorption aimed at making better medical implants and more sensitive biosensors. These include; grafted polymer layers[1], plasma polymerisation[2] and oligoethyleneoxide SAMs on gold.[3] However, the long term effectiveness of these approaches remain uncertain, therefore alternative methods are of great interest particularly those that can provide a better understanding of protein-surface interactions. Chemical patterning on the nanoscale is one way of generating surface regions with low concentrations of molecules and potentially provides a platform for probing functionality down to the single molecule level. One of the promising ways of generating nanopatterns is by decoration of surfaces with nanoparticles of different size and chemical functionality. Several methods have been developed to grow binary nanoparticle assemblies such as layer-by-layer (LBL) approaches[4] and one-step assembly. Here, we demonstrate a simple one-step process that generates ordered binary colloidal particles of different surface chemistry assembled on hydrophobic surfaces.

METHODS: The patterns are generated from either diluted or concentrated suspensions of poly(styrene) (PS) nanoparticles of different sizes (diameter = 500nm to 60nm), different size ratios and volume fractions, and different nanoparticle surface chemistry (sulfonated, carboxylated, or aminated). Si wafers and glass are made hydrophobic by modification with OTS (octadecyl tricholorosilane). In addition, adhesive carbon tape is used as a substrate. After preparing nanoparticles suspensions in McIlvaine's buffer with appropriate size ratios and volume fractions, droplets of 25 µl are placed on surface and the assembly process takes place over night under vacuum conditions. We use AFM and SEM to observe the nanoparticles assemblies formed after solvent evaporation.

RESULTS: Figures 1 A and B shows AFM height images of two component patterns formed using 60nm sulphated-PS and 350nm sulphated-PS nanoparticles on carbon tape and OTS modified glass substrate. This pattern consists of a hexagonally packed array of large particles with regularly inter-dispersed with the smaller particles. The patterns are formed independent of the surface chemistry of the particles (data to be presented).

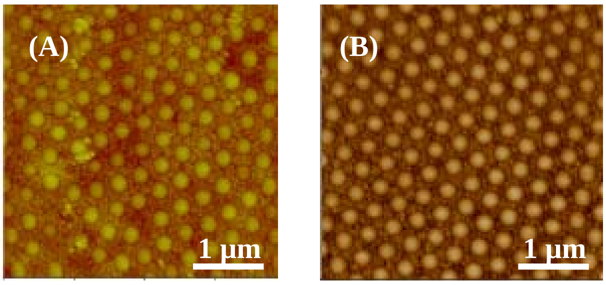

Fig. 1: Two-component patterning using 60nm sulfated-PS NPs and 350 nm sulfated-PS NPs (pH 7) on different substrates. (A) AFM height of a two-component colloid crystal assembled on carbon tape. Peak-to-peak distance was 351 nm. (B) Corresponding height images of hydrophobic glass (OTS-modified) Peak-to-peak distance was 355 nm

DISCUSSION & CONCLUSIONS: The patterns are formed by an entropically driven process upon drying where solvent evaporation increases the particle volume fraction to stage where it is high enough to induce colloid crystal formation. The surface is hydrophobic enough to prevent spreading of solvent. In short, we show that hexagonal structured pattern with two-components nanoparticles of varying size and volume fraction can be created by a simple drop-casting process and this provides us with a unique capability to manipulate both surface structure and chemistry at nanoscale level. This is of importance in order to understand and control interfacial phenomena, such as protein adsorption and directed immobilization, cell and bacterial adhesion, and controlled surface wetting in areas of biosensors, medical materials. Future work will involve taking advantage of the surface patterns to perform surface reactions with molecules that have improved functionality.

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