

Nanostructures fabrication via self-assembly of hybrid block copolymer/nanoparticles in thin film

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ABSTRACT

Hierarchical nanostructure of gold nanoparticles via self-assembled block copolymer have been investigated on native oxide-terminated Si(111). Au-nanoparticles were prepared via simple wet chemical method by using Poly styrene-block-4-vinylpyridin (PS-b-P4VP) as stabiliser in nonaqueous solvents. Transmission Electron Microscopy (TEM) is used to characterise the size of the Au-nanoparticles. However, the size distribution of Au-nanoparticles is found to be narrowly dispersed with dimension of 2-3 nm. Adsorption (via spin-coating) on hydrophilic surfaces results a necklace-like structure. Adding a nonpolar selective solvent (toluene) to one of the block copolymer leads to the formation of nanoporous morphology with two different diameters. Tapping Mode Atomic Force Microscopy (TMAFM) measurements on spin-coated thin film observed large holes (120 nm in diameter) surrounded with small porous ones with an average diameter of 25 nm. Solvent-evaporation from the surface to the interface with the substrate and dewetting of the block copolymer chains on substrate were found to be of great significance in the fabrication of the two different sizes of the nanoporous.

Keywords: Block copolymer, Nanostructures, Hierarchical Nanoporous, Au-Nanoparticles, Necklace-like structure, self-assembly.

1 INTRODUCTION

The synthesis of nanostructured material with tunable properties is the key to the developments of varying application in nanoscale science and technology. The ability of block copolymer for templating nanoparticles into nanostructured hybrid material [1, 2, 3] offers the potential to fabricate high-density arrays for use in data storage [4], electronics [5], and molecule separation [6]. A diblock copolymer molecule contains two distinct chemically polymer chains connected together with covalent bonds at their ends (microphase-separation). Therefore, these can self-assemble into different nanodomains morphology. The spacing between the domains and the morphologies (spheres, cylinders and lamellae) depends on molecular weight, volume fraction, and the strength of interaction

between the blocks as represented by the Flory-Huggins interaction parameter [7,8].

In thin film based on varying application, self-assembly of block copolymer is still insufficient (defects) to give a long-range of ordered nanostructures. Therefore, many methods such as external electric fields [9], solvent evaporation, shear force [10], temperature gradients [11], chemically pattern substrate [12] have been used to eliminate these defects. In an important recent development, several reports have demonstrated that different morphologies of block copolymer in particular cylinders morphology can be obtained normally orientated to the substrate surface over a large scales area via, for example, external electric field, solvent evaporation. Rather, they have been used as a nanotemplate to produce high-density nanorods arrays [13].

In this communication we demonstrate an effective route to prepare narrow distribution Au-nanoparticles in nonaqueous solvent. Adsorption (via spin-coating) on hydrophilic surfaces results in a necklace-like structure. However, adding a nonpolar selective solvent (toluene) for one of the block copolymers leads to the formation of a heterogeneous nanoporous structure of hybrid materials in thin film. The hybrid material based on noble nanoparticles orientated via self-assembled diblock copolymer at room temperature.

Block copolymers were recently extensively used to templating inorganic nanoparticles. The key function for templating nanoparticles via block copolymers is to form steric or ionic barriers around the nanoparticles to avoid the particles coagulation. Rather, the effectiveness in controlling particle size and size distribution of the nanoparticles. However, control the intercluster spacing by changing the length of the block copolymer tail. Deposition of the hybrid material on suitable solid substrate (via spin- or dip- coating) leads to form an ordered uniform nanodots [14, 15, 16, 17, 18].

The approach described here, is a simple route to prepare hybrid material system based on self-assembled Polystyrene-block-Polyvinylpyridine(PS-b-P4VP)stabilised Au-nanoparticles in nonaqueous solvent (DMF). The copolymer domains are involved to control the size and the size distribution of the Au-nanoparticles resulting in narrow size distribution of 2.5 nm. Adding a nonpolar selective solvent (toluene) for one of the block copolymers leads to form a uniform micells loaded with the Au-nanoparticles. Adsorbing mono micellar film via spin coating on SiO₂-

substrate forms a large area of ordered nanoporous arrays orientated normally to the substrate surface.

The novelty of this work is due to the forming of a necklace-like nanostructure. However, adding a nonpolar solvent leads to switching the structure into heterogeneous ordered nanoporous structure. This nanoporous morphology could be used as an effective template for other different metals [13,19].

2 MATERIALS AND METHODS

An asymmetric diblock copolymer of PS-*b*-P4VP was used in this study. The PS and P4VP had molecular weight of 41300g/mol and 1900 g/mol respectively (Polymer Sources Inc). The micelles were formed by dissolving 7 mg of diblock copolymer in 1 mL of dimethyl formamide (DMF). They were then loaded with 1.0 equiv. HAuCl₄ ([HAuCl₄]/ [4VP] = 1.0) and stirred for 1 h. A black solution was obtained after adding LiBH₄ as a reducing agent. By adding 1 ml of toluene, the block copolymer formed a micelle structure loaded with Au in core and surrounded with PS shell. Finally, the solution was spin coated onto native oxide-terminated Si(111) wafers, the thickness of the films was controlled by the spinning speed (3000rpm/min).

Transmission electron microscopy (TEM) studies were conducted using a JEOL 2000FX instrument operating at an acceleration voltage of 80 kV. Dilute solutions of the gold-labeled micelles were deposited on copper grids (400 mesh) that had been precoated with a thin film of Formvar (poly(vinylformal)) and then coated with carbon. The samples were applied to the grids and allowed to air-dry overnight.

AFM images were obtained in both height and phase contrast modes using a Digital Instruments Dimension multimode scanning force microscope in the tapping mode. Silicon tips on a cantilever (Nanoprobe) with spring constants ranging between 40.0 and 66.0 N/m (as specified by the manufacturer) were used.

3 RESULTS AND DISCUSSION

The structure and size distribution of the Au-nanoparticles particles have been analyzed by TEM. Figure 1 shows a typical overview image of the sample, together inset with HRTEM micrograph of an individual Au-nanoparticle with a corresponding Fast-Fourier-Transformation (FFT). The TEM micrograph reveals that the Au-nanoparticles have diameters in the range 2-3 nm. However, the existence of the lattice planes on the HRTEM images of the particle indicates high sample crystallinity as can be seen in the inset FFT.

Figure 2 is a histogram of the nanoparticle showing the size distribution, determined via direct measurement from the TEM images. The histogram was fitted using a Gaussian function. (Attempts to model the distribution with a log-normal function did not produce better fits).

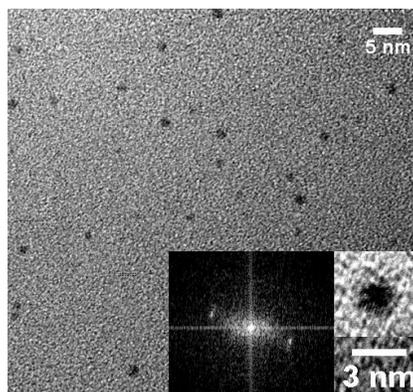


Figure 1: TEM images PS45-*b*-P4VP28 loaded with HAuCl₄ at molar ratio (4VP: Au 1:1). Inserts show a single Au-nano particle with the corresponding FFT.

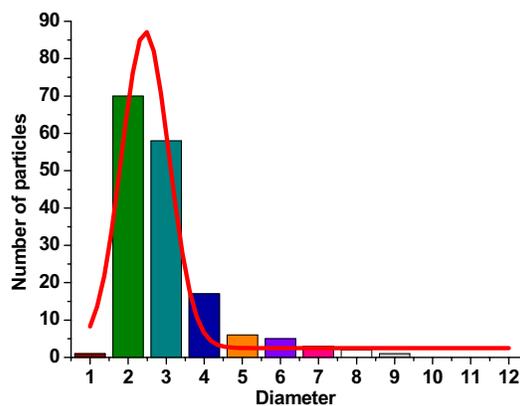


Figure 2: A histogram of nanoparticle diameters, as measured using TEM micrographs. A Gaussian fit yields a mean diameter of 2.4 nm and a standard deviation of 1.8 nm.

Figure 3 shows AFM image of PS-*b*-P4VP_{0.1}(Au_{0.1}) thin film deposited via spun casting from DMF solution on SiO₂ substrate. The image revealed an individual necklace-like morphology laying flat on the substrate with an average height of 25 nm and length of 700 nm.

It seems from the AFM images, that the Au-nanoparticles aggregate together in the copolymeric matrix. While the long PS tails in the block copolymer tend to aggregate in order to reduce the interfacial energy between the PS and the hydrophilic substrate as well as between the PS and air. By adding toluene to the hybrid solution in DMF, the diblock copolymer formed micelles that consists of P4VP(Au) in core surrounded with shell PS.

Figure 4 shows AFM height image of spin coated PS-*b*-P4VP_{0.1}(Au)_{0.1} hybrid block copolymer thin film deposited on SiO₂ substrate. An array of heterogeneous nanoscopic cylindrical domains oriented normal to the substrate, is seen at the surface of the film.

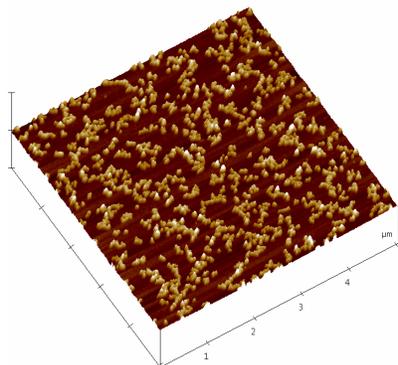


Figure 3: Tapping mode AFM images of PS-b-P4VP(Au) in nonaqueous solvent (DMF) spun casting on SiO₂-wafer. the 3D-image show necklace-like structure of Au-nanoparticles in polymeric matrix.

The cross sectional profile in fig 4 recorded across the AFM image, the depth of the nanoporous 25 ± 3 nm, and the film thickness was 50 nm. The image demonstrates different sizes of nanoporous morphologies. However, big holes (~120 nm) constantly surrounded with small porous (~25 nm). Solvent-evaporation from the surface to the interface with the substrate [20] and dewetting of the block copolymer chains on hydrophilic substrate were found to be of a great significance role in the fabrication of the two different sizes of the nanoporous structures.

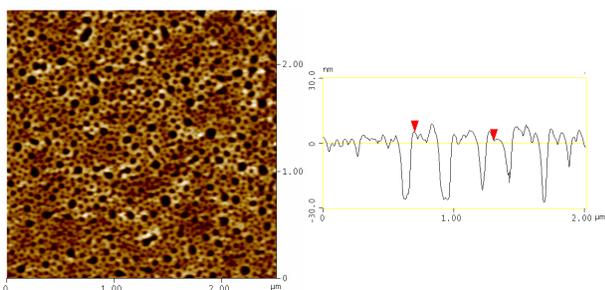


Figure 4: AFM height image of PS-b-P4VP_{0.1}Au_{0.1} film obtain by spin coating on SiO₂ substrate. The image shows cylindrical microdomains orientated normal to the film surface.

4 CONCLUSION

We have demonstrated that hierarchical nanostructures can be obtained using self-assembled hybrid material based on diblock copolymer. Narrow size distribution of Au-nanoparticles was prepared by using diblock copolymer in nonaqueous solvent. Direct deposition via spin coating on hydrophilic substrate has obtained a thin film of a necklace-like structure. Adding nonpolar solvent selective for one of the diblock copolymer forms a micelle structure.

Deposition of these micelles from this solution on hydrophilic substrate (using spin coater) can switch the structure from necklace-like into a heterogeneous nanoporous based on Au-nanoparticles in the copolymer matrix. We believe that such nanostructured materials could find application as sensors, membranes and could be used as nanotemplates for fabrication nanorods, and nanowires.

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