Fabrication and properties of nanoscale metallic arrays in polymers

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Abstract

Bottom up and top down approaches were explored for creating random and ordered metallic arrays in polymer matrix, respectively. For the bottom up method, the synthesis of Au, Pd and Ag nanoparticles stabilized by reverse micelles from an amphiphilic copolymer was performed. TEM images revealed partially ordered structures of Au nanoparticles with an average particle size less than 15 nm. In contrast, Ag and Pd were mostly disordered structures. Top down fabrication of Au features in PMMA were fabricated by milling with a focused ion beam. The features were about 50 nm in width with a 20 nm periodic spacing. The two approaches provide model systems for understanding the optical and electrical properties of nanostructured materials at 2 limiting extremes of order.

Keywords: nanoparticles, nanocomposites, reverse micelles, self-assembly.

1. INTRODUCTION

In the recent years, metals/polymers nanocomposites emerged as an important field in the nanotechnology and nanodevices due to their enhanced optical, thermal, electrical and catalytic properties. Our prior studies on the palladium/polycarbonate nanocomposites [1] showed that morphology of the nanoparticles determines the properties of the resulting nanocomposites. Similar structure-property relationships were noted by Chatterjee *et al* [2], Liu *et al* [3] and Wang *et al* [4] in the metal/polymer nanocomposites. In order to avoid agglomeration in nanocomposites, functionalized organic ligands [1, 5] or polymers [3, 4, 6, 7] have been employed as dispersing agents. Polymers have often been preferred over organic ligands due to the convenience in handling, reduced post-synthesis treatments and more direct applications.

Dispersions of metal salts in homopolymers have not been successful in achieving periodic nanostructures. However, a few recent studies [8] explored copolymer systems in the synthesis of periodic structures. In the present work, we explored a simplified route to synthesize self-assembled Au, Ag and Pd nanoparticles with an amphiphilic copolymer like PS_b_PEO as a stabilizing agent. PS_b_PEO was selected due to the presence of both hydrophilic and hydrophobic blocks which helps have been reported to aid the formation of periodic structures with nanoparticles. Focused ion beam milling was used to create Au nanoscale periodic arrays supported on silicon wafers. Polymethyl methacrylate was spun coated from solution to create nanocomposites from these patterned arrays. The two approaches are considered in turn.

2. NANOPARTICLE DISPERSIONS

All analytical grade chemicals used in the synthesis were purchased from Sigma-Aldrich USA. Deionized water with a resistivity of 18 x 10^6 Ω-cm was obtained from a Millipore unit. Lab synthesized diblock copolymers PS_b_PEO was used as such. The stepwise procedure followed in the atom transfer radical polymerization of PS-b-PEO polymerization is given elsewhere [Journal of applied polymer science, 2006. Vol. 102, pp. 4304-4313]. In the synthesis, 100 mg of powdered PS_b_PEO is dispersed into the acetone/water mixture. 1ml of 0.1M metal salt solution is slowly injected into the polymeric solution through micro-syringe. The metal salt solution is then reduced with a slow injection of 1M $NaBH_4$ to the reaction mixture. The reduction is accompanied by a drastic color change indicating the nanoparticles formation as shown in Figure 1. The copolymer stabilized metal nanoparticles were allowed to settle down. The acetone/water mixture is decanted and the nanocomposites sediments were washed thoroughly with deionized water. The nanocomposites were then dried and dispersed in toluene for further characterization. All steps were carried out under normal room conditions.

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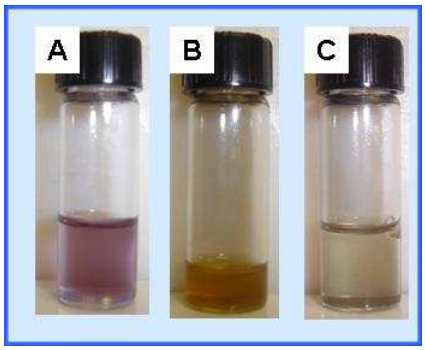


Figure 1: Nanocomposites dispersed in toluene; a. Au/PS_b_PEO b. Ag/PS_b_PEO c. Pd/PS_b_PEO

2.1 Optical Properties

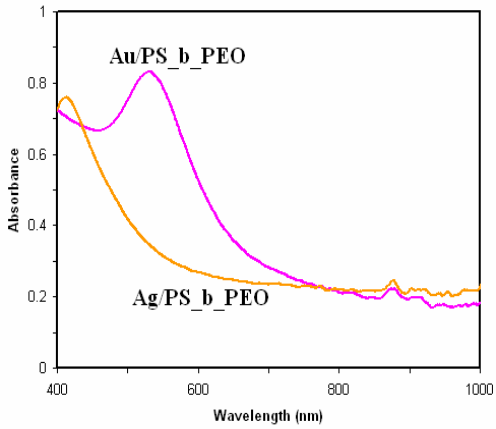


Figure 2: UV-Vis absorption spectra of Au and Ag nanoparticles.

As shown in the Figure 2, appearance of new absorbance peak at 530 nm and 420nm confirms the Au and Ag nanoparticles formation respectively. Similar results were noted by Liu *et al* [3]. Pd nanoparticles however failed to show any such characteristic peak as supported by the early studies on Pd/PMMA nanocomposites by Aymonier *et al* [6]. In the absence of PS_b_PEO all the reduced metal particles tend to settle down and form macro-sized powders that are found not dispersable in toluene. In the presence of PS_b_PEO, the metal nanoparticles tend to remain completely dispersed in toluene.

2.2 Morphology

Figure 3 shows the TEM images of metal/polymer nanocomposites. Au/PS_b_PEO and Pd/PS_b_PEO nanocomposites exhibited self-assembled nanoparticles of 15nm size. There have been very few prior studies reporting self-assembled metal nanoparticles when capped by a copolymer via wet method. Prior work by Moller *et al* [8] on Au/ PS_b_PEO, involved the drying of the metal salt-polymer mixture followed by an electronic reduction of metal salt. In the present work, the stability might be attained due to the reverse micelles from PS_b_PEO with PEO blocks (head) being the hydrophilic part while the PS (tail) is the hydrophobic part.

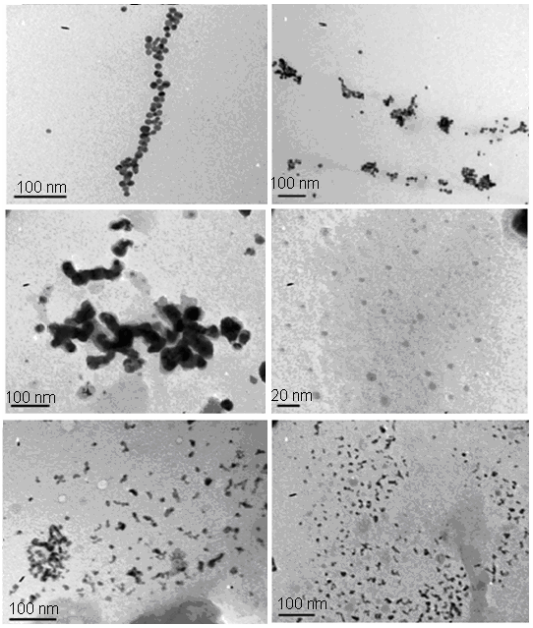


Figure 3: TEM images of (top) Au/PS_b_PEO (~15nm), (middle) Ag/PS_b_PEO (~5nm), and (bottom) Pd/PS_b_PEO (~10nm).

A schematic representation of metal nanoparticles adhering to the hydrophilic PEO blocks is shown in the Figure 4. Further FTIR and X-ray diffraction studies need to be performed to confirm the possible chemical interactions between the metal nanoparticles and the PEO blocks.

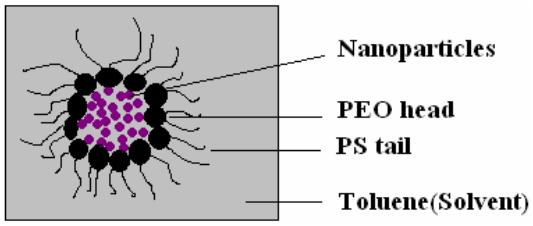
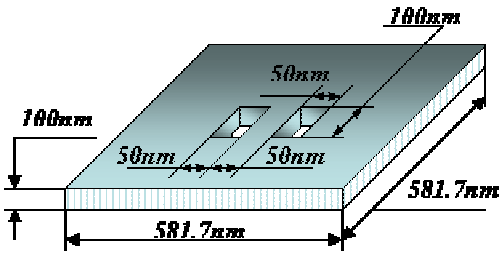


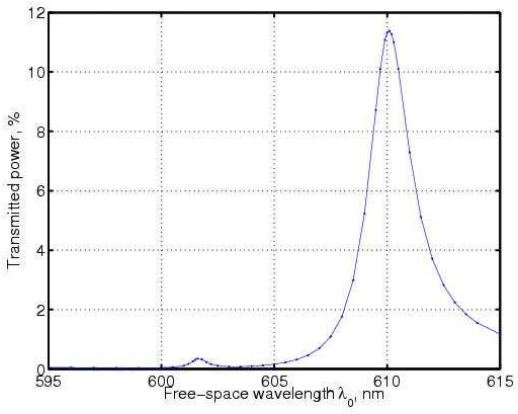
Figure 4: Schematic representation of capping of metal nanoparticles by the inverse micelles from PS_b_PEO

3. PERIODIC METALLIC ARRAYS

Controlling light at sub-wavelength scales is of considerable interest due to applications in broadband filters, sensors, substrates for miniature antennas, and sub-wavelength cavities. Metal-dielectric nanostructures have received attention due to their highly structure-sensitive optical properties and due to possibility to create various distributions of enhanced localized electric fields that allow for sub-diffraction-limit optical imaging. For example, a periodic arrangement of features (such as perforations in Figure 5A) yields frequency-dependent reflection and transmission properties (Figure 5B), which can be manipulated by changing the size, shape, and distance between the features. However, the challenges to produce such nanostructures remain.



A



B

Figure 5: Periodic nano-perforations in silver film and enhanced transmission predicted theoretically

Our principal objective is to design periodic nanostructures with requisite optical properties and develop the means by which they can be reproducibly fabricated with relative ease and adapted for various applications. To this end, we will use a recently developed, rigorous theoretical/numerical tool set by which we can systematically understand the physics of electromagnetic interactions of materials at nanoscale regimes. This approach will be used to develop design rules for nanocomposites with specified periodicity and nanoscale features with: (a) predictable frequency-selective responses to electromagnetic radiation and (b) predictable distribution of enhanced electric fields (antenna-like effects). Obtaining such material systems hinges on the availability of nanofeatures with accurately controlled size and shape attributes, and methods for arranging them into two and three-dimensional structures of uniform periodicity. The nanoscale periodic structures will be fabricated using two approaches: self-assembly and nanofabrication. Structure-property-processing relationships of these material systems and architectures will be developed to refine and validate the design rules.

In this study, we explored the focused ion beam milling technique for fabricating such structures. Furthermore, by systematic varying of the nanostructure parameters, we will be able to explore dependence of the optical properties on the nanoscale features of our structures and compare experimental findings with results of calculations.

3.1 Nanofabrication

An attractive proposition would be to have a possible device on Si for applications in integrating with opto-electronic devices. Our approach was to create polymer nanocomposites with periodic structures the focused ion beam machining of metal nanofeatures and embedding them in polymer monolayers using self-assembly. Ion beam patterning involves patterning based on Coulombic interactions between positively charged ions and charged electrons and nuclei of sample atoms. Initial structures were performed on transparent SiO_2 membranes on supporting Si skeletal structure (Figure 6).

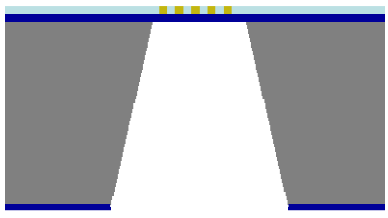


Figure 6: Schematic representation of periodic Au nanostructures on a SiO_2 membrane fabricated on a Si wafer

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An optical image of the membrane substrate for the nanofabricated structure is shown in Figure 7.

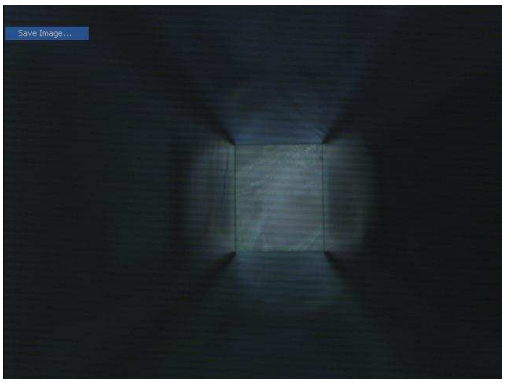

Figure 7: Top down view of a 100 µm square membrane formed on Si by etching

An optical micrograph of the patterned Au nanostructures on the membrane is shown in Figure 8.

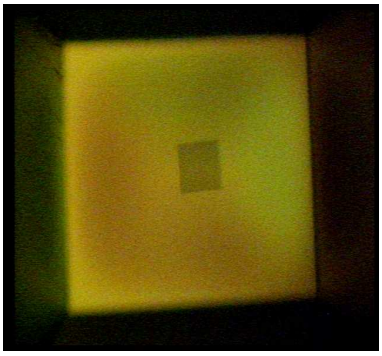

Figure 8: Optical image of a nano-patterned Au structure on oxide membrane.

The SEM image of the nanostructured patterns is shown in Figure 9.

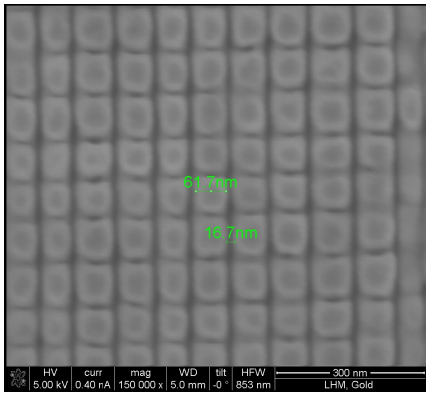

Figure 9: SEM view of nano-patterned grid showing a 61.7nm structure with 16.7nm spacing on an Au patterned sample.

The samples were characterized further by AFM to better understand the topographical details of the periodic structures (Figure 10).

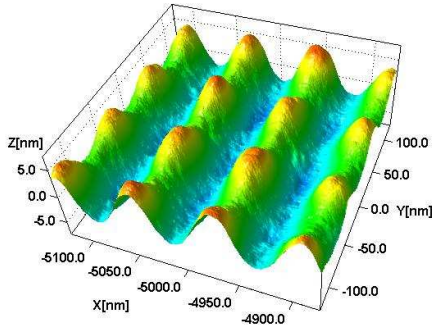

Figure 10: AFM characterization of patterns in the tapping mode rendered in 3D

In summary, a bottom-up approach based on nanoparticle synthesis in a block copolymer solution provided partially ordered to disordered structures in the present work. In contrast, highly periodic structures were obtained by top-down fabrication methodologies using ion beam milling as an example.

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