

Facile Assembly of Nanoparticles into 2D Micro-structured Films by a Polymer-aided Self-organization Process

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ABSTRACT

The self-assembly of micro- and nano-structures in periodic arrangement of distinct, uniform-sized nanocrystals are increasingly popular as a potential future alternative to conventional micro-fabrication techniques. One of the straightforward manipulations to periodic patterned structures is by polymer-aided self-assembly of nanoparticles. Herein the present study, we prepared micro-structured films of nanoparticles by exploring the ability of self-organization property of a tailor-made functional polymer. Our studies demonstrate that asymmetric amphiphilic poly(*p*-phenylene) directs the assembly of nanoparticles into a 2D micro-structured film, irrespective of the surface properties of the nanoparticles.

Keywords: Light-emitting films, amphiphilic PPPs, self organization, micro-structuring

1 INTRODUCTION

The eventual properties of nanoparticles are substantially dependant on the inter-particulate ordering and distance. As such, manufacturing nanoparticle-containing thin films with complex structures with long range lateral order and orientation via a top-down approach have been investigated by many research groups [1-3]. The bottom-up approach, not as vastly prevalent approach so far, makes use of self-organizing small units such as molecules, chains of polymer and nanoparticles, in which the morphology control only involves selection of choice of material and self-organization conditions. The latter method, inspired by nature systems [4-5], is currently being actively investigated by some researchers [6-9] to achieve desirable thin film configuration and properties. Subtle adjustments in environment conditions allow remarkable control in the consequent morphologies [9]. Herein we outline the fabrication of micro-structured blue light-emitting thin films of novel, functionalized amphiphilic poly(*p*-phenylene) (PPP) which is being investigated as a potential candidate for advanced polymer electronic and

optical applications. We demonstrate how this polymer is used as template to afford large area of periodic and intricately patterned conjugated thin polymer-nanoparticle hybrid films based on the breath figure method first reported by Francois [10]. Combining the distinctive property of the polymer, and unique electronic, photonic and catalytic properties of the nanoparticles, great potential in the development of many novel functional films can be realized.

2 EXPERIMENTAL DETAILS

The functionalized amphiphilic PPP was synthesized as previously reported [11] using Suzuki polycondensation of respective monomer and used for the present study. The chemical structure of asymmetrically functionalized PPP is shown in Figure 1. The incorporation a long alkoxy chain on one side and hydroxyl groups on the other side of the polymer backbone provided the desired amphiphilicity (Figure 1).

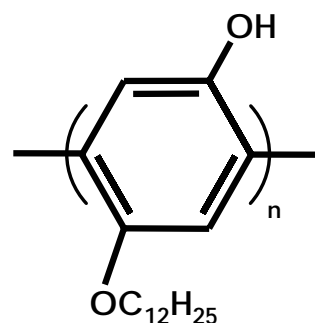


Figure 1: Chemical structure of PPP used.

The synthesis of dodecanthiol stabilized gold nanoparticles was carried out using a phase transfer from water to toluene reduction with sodium borohydride in the presence of the dodecanethiol as ligand [12]. Partial ligand exchange of the hydrophobic gold nanoparticles was carried out via 11-mercapto-1-undecanol exchange route using

previously reported method to alter the hydrophobicity of the nanoparticles [13]. All chemicals were purchased from Sigma Aldrich and used without further purification.

The polymer film was prepared by dropcasting of 0.5 mg/ml of polymer in chloroform in ambient conditions. Organic-inorganic hybrid films were similarly prepared with addition of required amounts of nanoparticles into the polymer solutions before spreading. The casted films were characterized as prepared, without further manipulation.

SEM images were taken with a JEOL JSM 6700 scanning electron microscope (SEM). The samples were carefully mounted on copper stubs with a double-sided conducting carbon tape and sputter coated with 2 nm platinum before examination. TEM images were taken using JEOL JEM 2010F at an accelerating voltage of 200 kV. The polymer and hybrid films were casted on MilliQ water and carefully transferred onto a 300 mesh copper grid for the TEM imaging. The I-V measurements were done using a 2-point probe via Keithley 237 High Voltage Source Measure Unit and LabVIEW data acquisition software.

3 RESULTS AND DISCUSSIONS

3.1 Morphology of polymer film

The morphology of the functionalized amphiphilic PPP is shown in Figure 2. It is apparent that the periodicity of the micro-structured honeycomb pattern spans over hundreds of square micrometers. The optimized alkoxy chain length and the phenoxy groups attached on the backbone of the polymer enables the polymer to remarkably stabilize water droplets during the film formation as described in the well-established breath figure method. The thickness and depth of the honeycomb walls are on average 650 nm and the pore size is 2.5 μm .

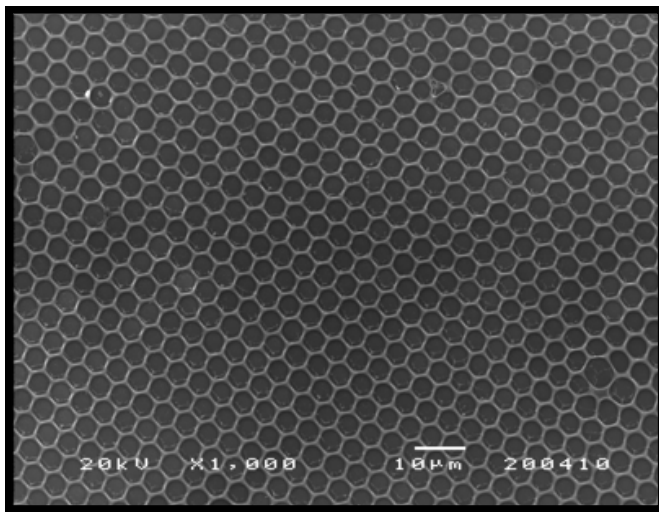


Figure 2: SEM image of micro-structured polymer film.

3.2 Morphology of nanoparticles

The TEM images of the gold (AuNPs) nanoparticles are shown in Figure 3. The nanoparticles have a low size distribution with diameters 3-4 nm. The ligand exchanged AuNPs did not have any observable change in size and morphology and is therefore not shown here.

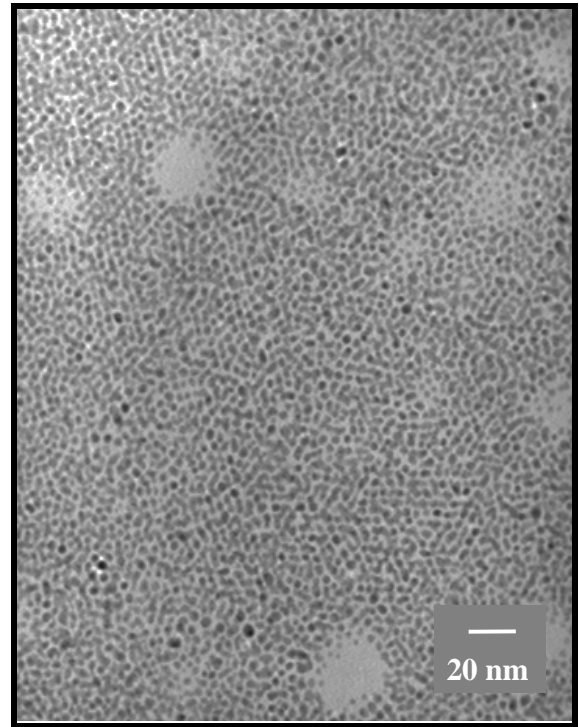


Figure 3: TEM images of gold nanoparticles.

3.3 Morphology of hybrid films

On progressive addition of the nanoparticles into the polymer solution prior to casting, relatively undisturbed self-organization was observed as apparent in the SEM analyses carried out on the samples.

The TEM images in Figure 3 of the hybrid films with different AUNP loadings show versatility of this direct micro-structuring technique. Both the polymer and the hybrid film can be casted on water and scooped onto any substrate of choice without substantial loss in the ordering of the films.

The pore sizes of the honeycomb cavities are slightly reduced as the AuNP loading were increased. This reduction in size is caused by the increased hydrophobicity of the thin films. The condensed water droplet size decreased hence influencing the pattern dimension.

4 CONCLUSIONS

It has been demonstrated that different nanoparticles can be micro-structured into a long-range lateral ordered films with excellent spatial distribution. The excellent ability of the tailored amphiphilic conducting polymer to self-organize into such highly ordered intricate thin films can be utilized as a 2D template to regulate the assembly of metallic nanostructures. This straightforward well-established breath figure method was modified by manipulating the content of casting solution thus enabling multiple hybrid organic-inorganic films without the need of costly instruments. These new hybrid films can be used in non-lithographic device applications, presently progressing in our laboratory

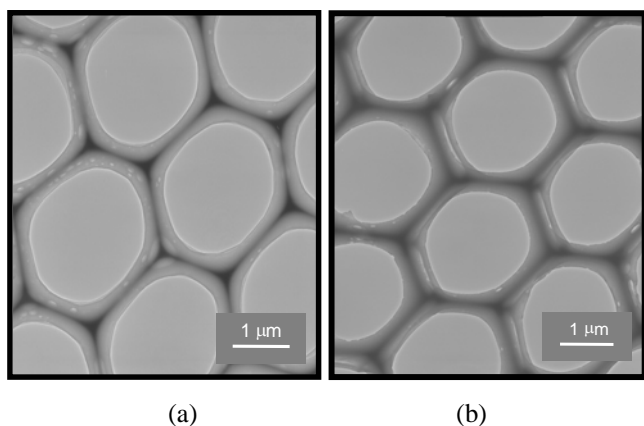


Figure 4: TEM images of micro-structured hybrid films with different nanoparticle loading w.r.t polymer content. (a) 5%, (b) 100%

The reduction in hydrophobicity of the AuNPs similarly did not disturb self-organization of the films. As shown in Figure 5 below, the AuNPs with the dodecanethiol ligand partially exchanged with the mercapto undecanol ligand showed retained spatially well-distributed nanoparticles within the internal walls of the micro-structured film. The hydrophilicity of the nanoparticles is not substantial enough to create a preferential self organization of the nanoparticles on the walls of the honeycomb as previously reported [14].

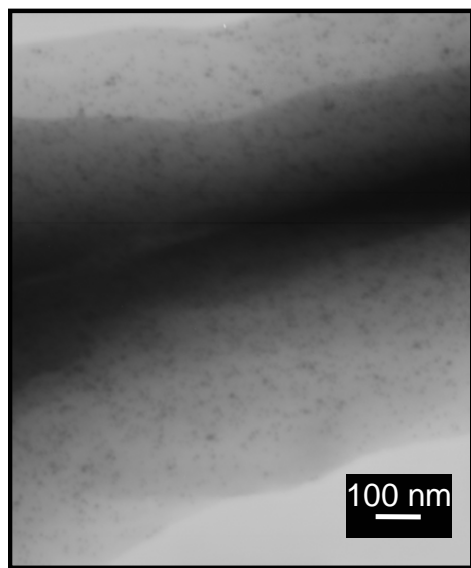


Figure 5: SEM image of hybrid film with 20% loading of ligand exchanged AuNP film. The inset shows TEM image a wall of honeycomb

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