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Impact of concentration and capping ligand length on the organization of metal nanoparticles in Langmuir-Blodgett surface micelles and nanostrands

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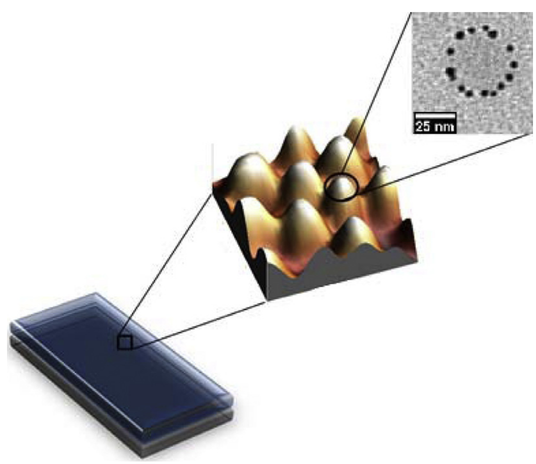
HIGHLIGHTS

- Block copolymers as templates for nanoparticle ordering at the air-water interface.
- Organization of metal nanoparticles into clusters, rings and lines over large surface areas.
- Effect of the capping ligand length on particle arrangement.
- Effect of particle loading on film morphology.

GRAPHICAL ABSTRACT



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ABSTRACT

Ultra-thin composite films have been prepared by the dispersion and organization of plasmonic nanoparticles in block copolymers. Polystyrene-*b*-polyvinylpyridine can be spread at the air-water interface to form periodic nano-domains with either a micellar or a lamellar morphology, providing an ordered template for the controlled assembly of metal nanoparticles. The exact spatial distribution of gold or silver nanoparticles of a fixed size (6 nm) is effectively controlled by the length of chemisorbed alkanethiol ligands. With this approach three types of nanoparticle assemblies can be obtained: clusters, rings and lines.

1. Introduction

Scientific interest in nanomaterials and nanotechnologies has dramatically increased in recent years. Among the large number of nano-objects currently being studied, metal nanoparticles [1] (NPs) have received much attention because of their unique optical properties. Upon irradiation, metal NPs behave as electrical dipoles that can absorb and scatter light [2]. When particle dimensions are significantly smaller than the wavelength of incident light, collective oscillations are induced in the conduction electrons of the metal, giving rise to the so-called localized surface plasmon (LSP). The surface plasmon is considered as one of the most effective

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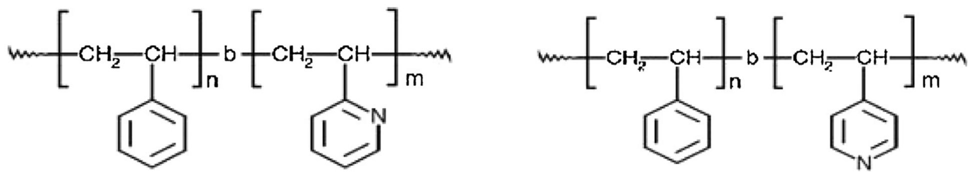

Fig. 1. Chemical structure of poly(styrene)-*b*-poly(2-vinylpyridine) (PS-*b*-P2VP) (left) and poly(styrene)-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP) (right).

light-matter interactions and allows for the manipulation of electromagnetic waves below their diffraction limits [3]. The plasmonic properties of metal NPs offer significant potential for applications in a variety of devices, such as biosensors [4,5] and waveguides [6–9].

Importantly, the characteristic frequency of the LSP is a function of several parameters, including the nature of the metal, particle size [10] and shape [11], the refractive index of the surrounding environment [12] and the precise way in which the NPs are organized [13–15]. With this in mind, ultra-thin composite films have been prepared in which the two-dimensional arrangement of plasmonic NPs is directed by a block copolymer (BC) template. BCs consist of two chemically distinct fragments that are covalently bonded together. When the blocks are immiscible, periodic nanodomains can appear [16]. Therefore, BCs represent a simple and reproducible way for the development of ordered nanomaterials [17,18].

In the present study, two-dimensional composite films containing metal NPs are prepared by the Langmuir-Blodgett (LB) technique. Through this bottom-up approach [19], we have prepared a variety of ordered NP assemblies covering relatively large surface areas, without the constraints of the tedious manipulation of individual nano-objects.

Although the self-assembly of inorganic NPs within BC matrices has already been investigated [20–25], very few reported studies employ the LB technique to form monolayer composite films [26–28]. We previously reported the organization of metal NPs within the surface micelle morphology of an amphiphilic BC [29]. Here, we extend this investigation to a related system that, in addition to surface micelles, presents a less common lamellar morphology [30]. In this way, the versatility of the LB approach is demonstrated through the preparation of self-assembled clusters, rings and strands of metal NPs.

2. Experimental methods

2.1. Materials

The BCs selected for this study are composed of a hydrophobic segment of poly(styrene) (PS) and a hydrophilic segment of poly(vinylpyridine) (PVP). Two different polymers were employed and their structures are provided in Fig. 1.

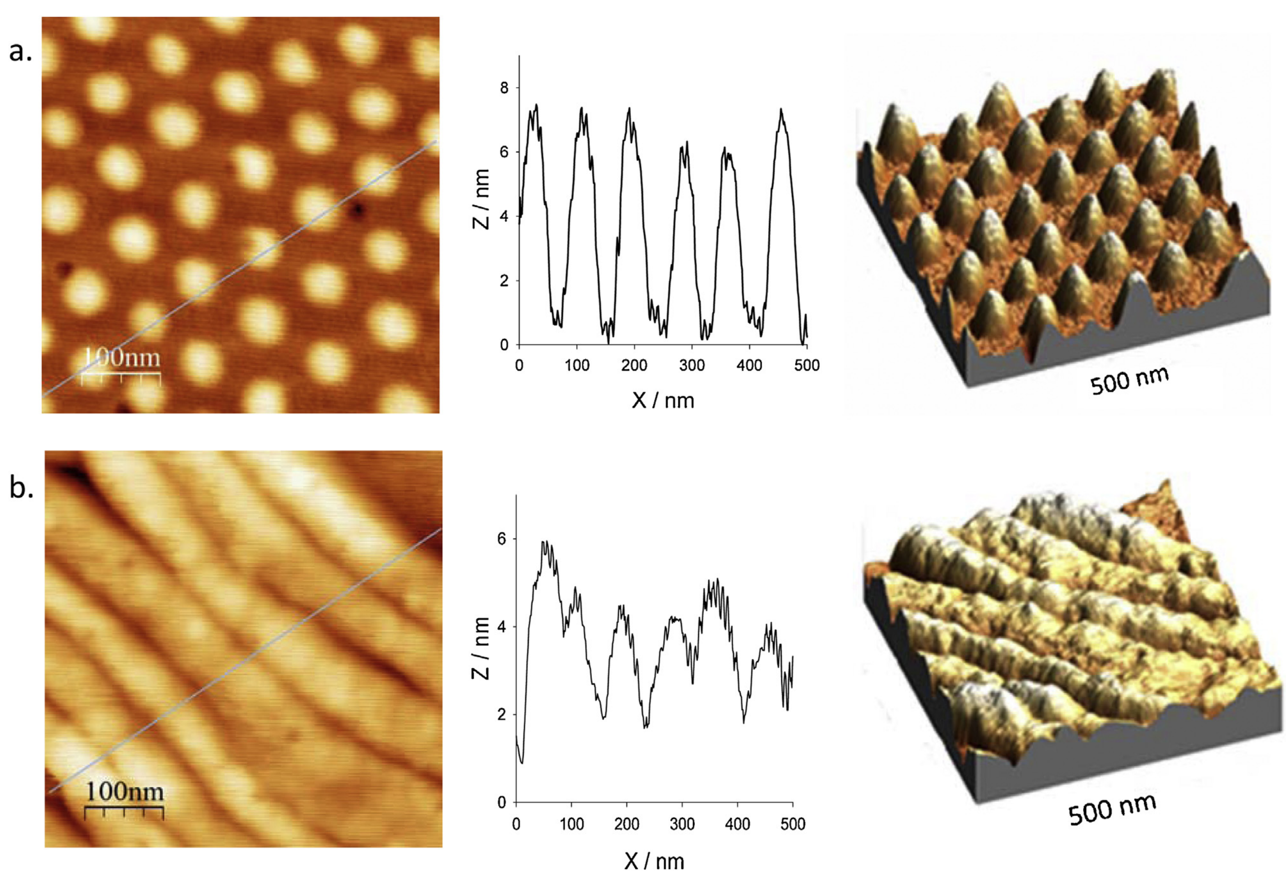

Fig. 2. AFM images and height profiles of BC LB films formed by spreading from chloroform solution (100 μL, 1.8 mg/mL) and transfer to glass at a surface pressure of 15 mN/m. Surface micelles (a) are formed by PS-*b*-P2VP whereas a lamellar (b) morphology is obtained with PS-*b*-P4VP co-spread with PDP.