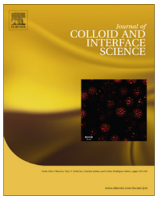
Journal of Colloid and Interface Science 443 (2015) 131–136

Contents lists available at ScienceDirect

Journal of Colloid and Interface Science

www.elsevier.com/locate/jcis



Assembly of polystyrene-coated gold nanoparticles at the air–water interface

Samuel S. Lamarre, Hélène Yockell-Lelièvre, Anna M. Ritcey *

Département de chimie and CERMA, Université Laval, Pavillon Alexandre-Vachon, 1045, avenue de la Médecine, Québec, Québec G1V 0A6, Canada

ARTICLE INFO

Article history:
Received 29 August 2014
Accepted 2 December 2014
Available online 9 December 2014

Keywords:
Gold nanoparticles
Block copolymers
Langmuir–Blodgett films
Self-assembly

ABSTRACT

Gold nanoparticles (NPs) coated with thiol-terminated polystyrene chains of varying molar mass were added to polystyrene-*b*-polymethylmethacrylate (PS-*b*-PMMA) block copolymer monolayers at the air–water interface. Composite films were transferred to solid substrates by the Langmuir–Blodgett technique. For most of the investigated systems, TEM micrographs and AFM images reveal the formation of 2D island-like aggregates of particles organized on a close-packed hexagonal lattice. This characteristic aggregate formation is lost when PS ligands are within the same length regime as the PS block from the copolymer. The results are compared with those obtained for analogous systems containing no copolymer where NPs are deposited on either a bare water surface or bare glass. Interparticle distance between NPs is found to depend on the surface on which they are deposited, the presence or not of the copolymer monolayer, and ligand length.

1. Introduction

The patterning of metallic nanofeatures on different surfaces is a growing trend in nanoscience research [1,2]. Two dimensional systems in which nanoparticle (NP) localization can be fine-tuned are important for the study of fundamental phenomena such as plasmonic coupling between metal nanoparticles. The precise control of nanoparticle placement in different architectures is also of practical importance and is key to the optimization of various devices such as solar cells [3–7] and sensors [8,9]. For example, NP sensing strategies based on surface-enhanced Raman spectroscopy, metal-enhanced fluorescence and surface plasmon resonance are all sensitive to details of particle organization at the nanoscale [10].

To date, the most efficient and reliable methods for the fabrication of ordered NP arrays on a substrate are top-down techniques, such as electron beam or ion beam lithography [11]. However, top-down patterning has intrinsic disadvantages such as the minimal size of the attainable features and a high cost per unit area nanopatterned. On the other hand, bottom-up techniques have always attracted interest because they are low cost, are able to cover large patterned areas and are not time consuming. In this paper we investigate a promising bottom-up way to pattern colloidal Au NPs on a solid substrate, namely Langmuir–Blodgett (LB) transfer. To achieve patterning in a Langmuir film, NPs are co-deposited at the air–water interface with chemical species known to adopt ordered morphologies at the nanoscale level. Composite Langmuir monolayers made of fatty acids mixed with various NPs have been previously studied [12–14]. However, the objective of the present work is to add a level of order to the NP films through the use of an amphiphilic block-copolymer [15–18]. More specifically, this study focuses on a class of diblock copolymers known to form circular nanodomains, known as surface micelles, when spread at the air–water interface [19–25]. Surface micelles are typically formed by symmetric block copolymers that contain a hydrophobic segment and a hydrophilic, non-water soluble block, such as the poly(styrene)-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) employed here. When PS-*b*-PMMA is spread at the air–water interface, the hydrophobic PS segments aggregate to form hemispherical domains that constitute the core of the surface micelles. The PMMA chains spread at the air–water interface as a pseudo-monolayer that both lies under the PS domains and forms a corona around them.

The NPs selected to be included in the PS-*b*-PMMA matrix are composed of a gold core decorated with thiol-terminated PS chains. Gold NPs are of interest to our group for their plasmonic properties [26,27]. While the literature covering composite films of block copolymers and NPs is very large, only a few experiments,

---

* Corresponding author. Fax: +1 418 656 7916.
E-mail address: anna.ritcey@chm.ulaval.ca (A.M. Ritcey).

http://dx.doi.org/10.1016/j.jcis.2014.12.009
0021-9797/

to our knowledge, have been conducted at the air–water interface. Cheyne et al. [28,29] successfully incorporated PS-coated cadmium sulfide quantum dots into 1D poly(stryrene)-*block*-poly(ethylene oxide) structures at the air–water interface and were able to transfer the resulting composite films to solid substrates by the LB technique. Li et al. [30] mixed iron oxide (Fe_2O_3) NPs with a poly(ethylene oxide)-*block*-poly(isobutylene) and reported either NP dispersion or NP aggregation, depending on the number of particles incorporated within the Langmuir film. We recently reported the use of PS-*b*-PMMA surface micelles as a template for the controlled 2D assembly of alkanethiol capped gold NPs [31]. The way in which the NPs organized within the polymer matrix was found to depend on both particle size and ligand length. The present study extends this work to investigate the assembly of NPs that are coated with polymer chains of the same chemical composition as one of the copolymer blocks. The results presented below indicate that PS-capped NPs exhibit behavior that is significantly different from that of their alkanethiol-capped counterparts. Furthermore, particle assembly is found to depend on the nature of the substrate surface, with the densest arrays being obtained with the LB technique. The results presented below indicate that the Langmuir–Blodgett technique can be used to prepare well-separated, island-like arrays of ordered metal NPs that are of potential interest for sensing applications based on plasmon enhancement.

2. Materials and methods

2.1. Au NP synthesis and functionalization

Gold cores of two different sizes were obtained by different synthetic routes. The smaller ones ($r = 2.7$ nm) were synthesized via a phase-transfer reduction method derived from Brust [32]. Larger particles ($r = 5.5$ nm) were prepared by citrate reduction in an aqueous medium. Both NP populations were functionalized with thiol-terminated polystyrene chains via a ligand transfer reaction. In all, nine thiol-terminated PS samples of different chain lengths were used to functionalize the gold cores: 3770, 4300, 6500, 8000, 8700, 12 700, 23 000, 43 000 and 66 000 g/mol. Experimental details concerning the preparation of the NPs, the synthesis of the thiol-terminated PS and the ligand exchange procedure are provided elsewhere [33].

2.2. Copolymer

A PS-*b*-PMMA block copolymer, with a mean molecular weight of 50 000 and 54 000 g/mol for the PS and the PMMA blocks, respectively, was obtained from Polymer Source Inc. (Montréal, Canada).

2.3. LB isotherms

Composite monolayers were obtained by co-spreading the copolymer and PS-coated gold NPs at the air–water interface from a single solution in HPLC grade chloroform (Laboratoires MAT Inc., Québec, Canada). PS-*b*-PMMA concentrations ranged from 0.7 to 1.2 mg/mL, whereas NP concentrations varied from 0.3 to 2.9 mg/mL, depending on the size of the gold core and the chain length of the ligand. Solutions were deposited dropwise, in a grid pattern, on Nanopure water in a KSV 3000 Langmuir trough. Spreading volumes varied from 55 to 100 μL. Exact concentrations and spreading volumes for each sample are provided as supporting information. After a delay of 5 min to allow for solvent evaporation, the monolayer was symmetrically compressed by two mobile barriers advancing at a speed of 1 mm/min.

2.4. LB transfers

Monolayers were spread as described above and compressed to a target surface pressure of 17 mN/m before transfer. Monolayers were transferred to glass microscope cover slips (Fisher Scientific) during vertical withdrawal at a speed of 0.5 mm/min. NPs spread alone on the water surface were transferred at a 0 mN/m surface pressure. Transferred Langmuir monolayers were imaged by transmission electron microscopy and atomic force microscopy.

2.5. Transmission electron microscopy

Monolayers were transferred onto carbon coated TEM grids, glued to glass substrates. TEM images were obtained with a JEOL 1230 microscope operated at 80 kV. TEM image analysis was carried out with ImageJ software.

2.6. Atomic force microscopy

AFM analysis was carried out with a Digital Instruments NanoScope MultiMode in tapping mode. Silicon cantilevers (MikroMasch) with a typical resonance frequency of 325 kHz and a force constant of 40 N/m were used. Tips had a radius of curvature of 10 nm.

3. Results and discussion

3.1. Block copolymer – NP composite films

In all, 18 different particle populations were investigated. Since the qualitative morphology of the system doesn't change for PS ligands with molecular masses ranging from 3770 to 43 000 g/mol, the general features of the composites will be discussed only for NPs coated with 12 700 g/mol PS chains. TEM and AFM images of composite films are presented in Fig. 1 for the two different particle sizes. In both cases, the NPs form 2D circular island-like aggregates. The average diameter of the island domains varies considerably with both particle size and ligand length (see Table S3 of Supporting Information). Comparison of domain size with various experimental parameters indicates that it can be correlated with the absolute quantity of NPs deposited, but this feature was not investigated in detail. Within the aggregates, NPs are arranged in an ordered close-packed 2D hexagonal lattice. Furthermore, larger NPs are found to concentrate in the center of the aggregates whereas smaller ones are relegated to the periphery. This size fractionation is due to the increase in the strength of van der Waals attractions with increasing particle size, leading to larger NPs serving as the primary nucleation sites for the formation of clusters [34].

The PS-*b*-PMMA monolayer morphology in itself is not significantly altered by the presence of NPs. The organized array of PS domains appears in both the TEM and AFM images of Fig. 1 and has the same characteristics as that observed in the absence of NPs. These observations suggest that the island-like NP aggregates are formed upon deposition of the spreading solution whereas PS domains are formed during compression of the monolayer, as they would in a non-composite monolayer [34].

This behavior differs significantly from that found for an analogous system, composed of NPs of similar size, but coated with alkanethiols rather than PS chains [31]. As reported elsewhere, alcanethiol coated particles adopt an organization dictated by the block copolymer, with the preferred location of the particles within the block copolymer template depending on both nanoparticle size and the length of the aliphatic capping agent.