

# Assembly of Ordered Polystyrene Nanoparticles on Self-Assembled Monolayers

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**Abstract:** Spontaneous assembly of nanoparticles onto a surface is a promising bottom-up concept for the fabrication of new functional materials that can be used for various applications in the nanotechnology. In this paper, we describe a system based on gold/polystyrene (Au/PS) Janus particles arranged onto Au self-assembled monolayer (SAM) of 1-dodecanthiol (NDA). The micro-size Au/PS Janus particles are self-assembled onto Au surface and are dissolved into polystyrene (PS) nanoparticles. The SAM of NDA plays two different roles; it dissolves the original Au/PS Janus particles and organizes the PS nanoparticles onto the Au surface. Overall, our proposed method for the assembly of large-scale area nanoparticles can be extended for further uses in the surface science.

**Keywords:** Self-assembled monolayer, Polymeric nanoparticles, Spontaneous arrangement, Polystyrene, Surface chemistry, Janus particles.

## 1. INTRODUCTION

The ability to order and self-assemble Micro-sized and nano-sized particles into well-defined shapes onto a surface is crucial for the development of various devices in the nanotechnology. Assembly of nanoparticles is a well-known bottom-up approach for the production of functional materials with complex structures, leading to a variety of materials that are of interest for many applications, such as nanoelectronics, biosensing and photovoltaics devices [1-4]. Overall, there are many different techniques to self-assemble nanoparticles, usually rely on one of two principles. The first is based on the molecular interactions between nanoparticles and surfaces, and the second is based on the use of external direction forces [5]. Arranged structures of nanoparticles allow control over the production of nano-sized materials with unique optical, magnetic, and electronic properties. Controlled organization of nanoparticles can be accomplished by different methods such as lithography [6-9], metal-mask methods [10], and chemical templates [11, 12]. However, any assembly process must allow control over the surface coverage, the particle distance, and the symmetry of the nanoparticles. All of those parameters determine the properties of the final nanostructures.

In recent years, self-assembled and spontaneous arrangements of nanoparticles onto different surfaces

have been found to play an important role in nanotechnology [13]. One of the most available method for obtaining an organized surface of nanoparticles is to use self-assembled monolayers (SAMs) [14]. The SAMs can be highly used to control over the assemblies of metallic nanoparticles [15, 16]. The uses of SAMs in controlled nucleation and growth is also demonstrated using biomimetic synthesis and in biomineralization process [17]. However, the use of SAMs for the assembly of polymeric nanoparticles, or for the preparation of polymeric surfaces, is quiet partial in the literature [18-20].

In this paper, we report on a new method for the preparation of ordered surfaces of polystyrene (PS) nanoparticles. Our method is based on a dissolution process of micro-sized Janus particles by SAMs of 1-dodecanthiol (NDA). Overall, Janus particles [21] are hemispheres particles containing at least two different surfaces, and are usually used as materials for advanced applications [22]. Some of the known Janus particles are systems of polymeric colloids [23], bimetallic [24], and systems of silica/metallic [25, 26]. In this work, we used Janus particles that are based on micro-sized PS particles, coated with Au thin film. The Au half-coated surfaces are designed in order to protect the PS particles from a fast dissolution.

Our new method for achieving highly ordered surfaces of nanoparticles is interesting for the fabrication of hydrophobic surfaces and for reducing wettability in different applications such as solar cells, microfluidics and glass covers [27, 28].

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## 2. MATERIALS AND METHODS

### 2.1. Preparation of NDA SAMs on Au Substrate

Au (99.995%) layer was sputtered onto mica ( $\text{KAl}_2(\text{AlSi}_3\text{O}_{10})(\text{OH})_2$ ) substrate under a high-vacuum (100 nm thick). The pressure was set for  $1 \times 10^{-3}$  mbar with a deposition rate of  $0.5 \text{ nm s}^{-1}$ . The as-prepared Au-Mica surfaces were found to be smooth with an average roughness (RMS) of ca. 7 Å and a typical Au films with a thickness of 100 nm. Moreover, the XRD measurements of the Au films demonstrated a strong crystal orientation along the (111) plane. The SAMs of 1-dodecanthiol were formed on the Au surfaces by immersing the Au substrates overnight in 10 mM NDA ethanol solution. After removal from the dispersion, the NDA SAMs surfaces were washed for three times with ethanol and were dried under a nitrogen flow.

### 2.2. Synthesis of Micro-Sized PS Particles

Non-cross linked PS particles (with a mean diameter of  $1.65 \mu\text{m}$ ) were prepared according to a previous protocol [29, 30]. Briefly, a mixture of ethanol (150 mL) and 2-methoxyethanol (62.5 mL) containing PVP, MW 360,000 (3.75 g, 1.5% w/v of total solution) was stirred at  $73^\circ \text{C}$  under a nitrogen environment for 15 minutes to exclude air. Next, solution containing the initiator benzoyl peroxide (1.5 g, 0.6% w/v of total solution) and styrene (37.5 mL, 16% w/v of total solution) was added to the reaction flask. The polymerization reaction was allowed to stand over 24 hours under a nitrogen flow. The formed microspheres were washed by extensive centrifugation cycles with ethanol and then with water. The particles were then dried by lyophilization.

### 2.3. Preparation Au/PS of Janus Particles

The Au/PS Janus particles were prepared based on a previously published procedure [31, 32]. In general, a layer of PS particles was produced by dripping 1:2 (v/v) water/isopropanol dispersion of PS ( $1.65 \mu\text{m}$ , 1% wt) onto a glass substrate. Subsequently, 100 nm of Au layer was sputtered onto the 2D ordered PS particles, at a pressure of approximately  $1 \times 10^{-3}$  mbar with a deposition rate of  $0.5 \text{ nm s}^{-1}$ . The obtained Au/PS Janus particles were removed from the glass-slide by sonication in ethanol for 60 seconds.

### 2.4. Binding NDA to the Janus Particles

The Janus particles were left to stand for 24 hours in an as-prepared 10mM NDA ethanol solution to

produce the binding of NDA on their surface. Next, the excess of NDA was removed from the dispersion by centrifugation at 2000 rpm for 10 minutes. The produced particles were then dried by lyophilization.

### 2.5. Assembly of PS Nanoparticles onto Surface

The Au substrate with 10mM NDA SAMs was stirred for 24 hours in a 20 ml ethanol solution containing Au/PS Janus particles to yield the organized surface.

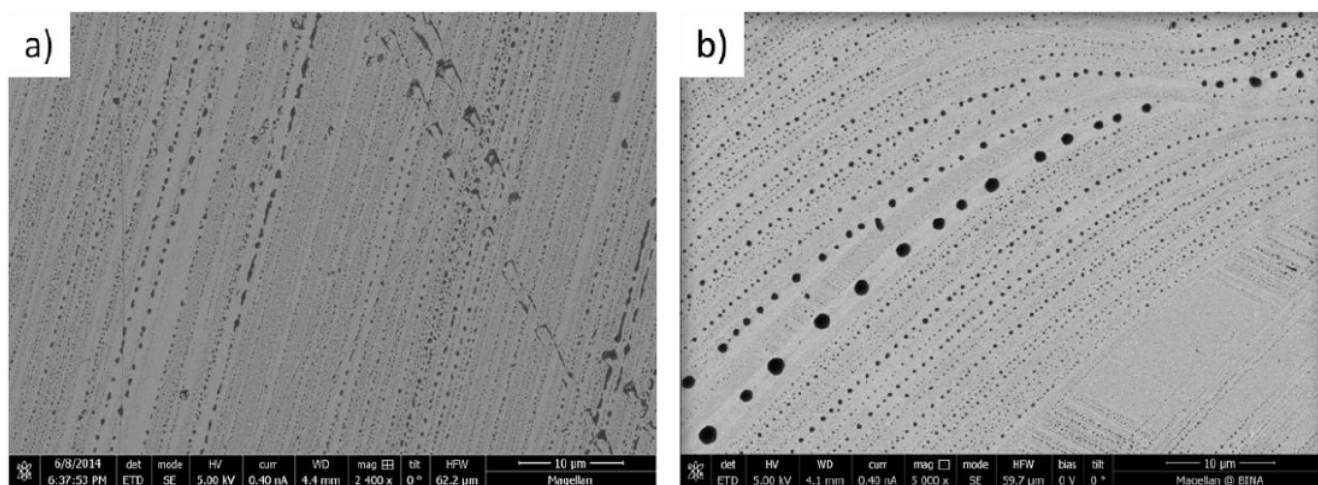
### 2.6. Characterization Techniques

The mean diameter of micro-sized and nano-sized particles was studied by dynamic light scattering (DLS) (PCCS, Nanophox particle analyser, Sympatec GmbH, Germany), and by statistic calculation of the particles mean diameter from High resolution scanning electron microscope (HR-SEM) images. The HR-SEM images and energy-dispersive X-ray spectroscopy (EDS) mapping were taken with an FEI (model Inspect S). All atomic force microscope (AFM) images and Micro-Raman spectra were performed using a dual microscope from Nanonics-Imaging which was free-space coupled to a LabRam HR Micro-Raman microscope from Horiba Jobin Yvon. X-ray photoelectron spectroscopy (XPS) was performed in a Kratos AXIS-HS spectrometer, using a monochromatized AlK $\alpha$  source.

## 3. RESULTS AND DISCUSSION

The structure of the NDA SAMs surface was analyzed by XPS, contact angle and ellipsometry measurements. The XPS results confirmed typical Au (4f) 85 eV, C (1s) 285 eV and sulfur (S 2p) 168eV peaks (attributed to the formation of S–Au bond). The ellipsometry measurements showed a layer thickness of 2 nm. The contact angle between a drop of water ( $3 \mu\text{L}$ ) and the substrate was measured and it was found that the contact angle of water ( $3 \mu\text{L}$ ) with Au-Mica substrate was  $73.3^\circ$ , whereas the contact angle of the NDA SAMs substrate increased to  $98^\circ$  indicating the formation of a homogeneous NDA SAMs. Next, we studied the formation of the ordered surfaces of PS nanoparticles onto the NDA-Au surfaces, and the contact angle was increased up to  $129.5^\circ$ , indicating a suitable value for hydrophobic surfaces [33-36].

HR-SEM images of the self-assembled PS nanoparticles onto the NDA-Au surface demonstrated a dashed-line assembling. The size distribution of the decomposed PS particles was in the range of 500 nm –

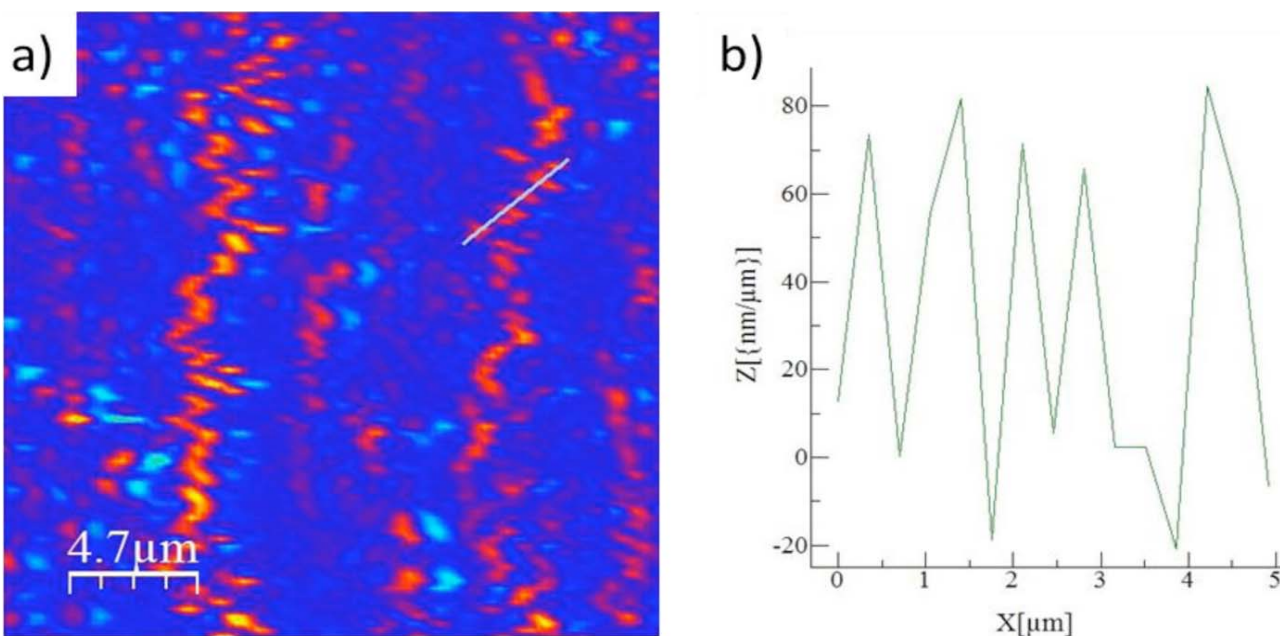


**Figure 1:** HR-SEM images of the assembled PS nanoparticles in two different areas of the NDA-Au surface (a and b). Scale bar=10  $\mu\text{m}$ .

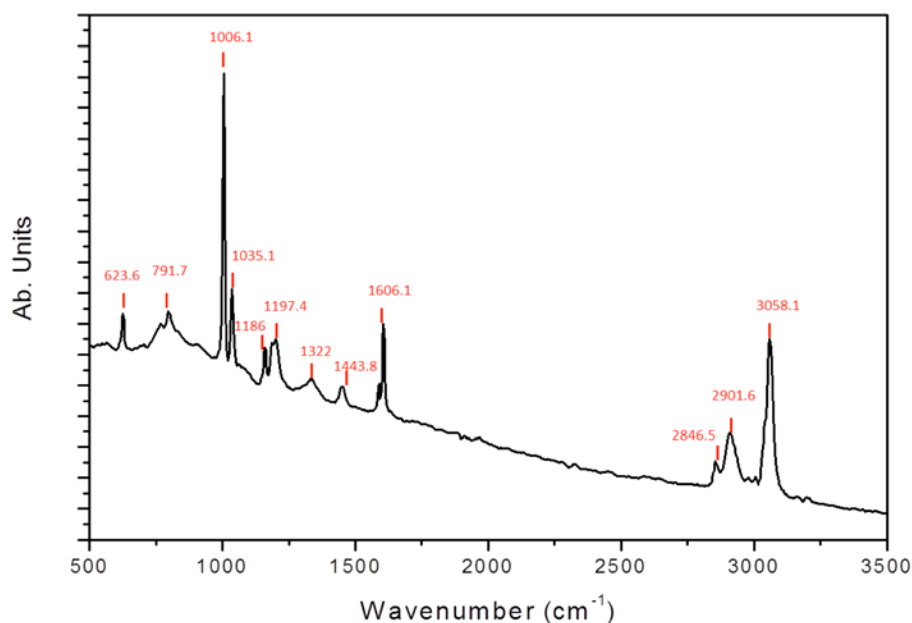
900 nm (Figure 1). For PS particles from the same array, the gaps were relatively constant, and their size distribution was narrow (under 10%). The distance between PS particles from the same array varied from 400 nm to 4  $\mu\text{m}$  and correlates to their size; smaller particles confirmed lower particles distance. Overall, the produced structure demonstrated a large-scale ordering of particles on a surface.

The AFM image (Figure 2a) and a height profile (Figure 2b) of the self-assembled PS nanoparticles revealed a characteristic height of around 80 nm-100 nm, and an inter-particle distance of about 200 nm.

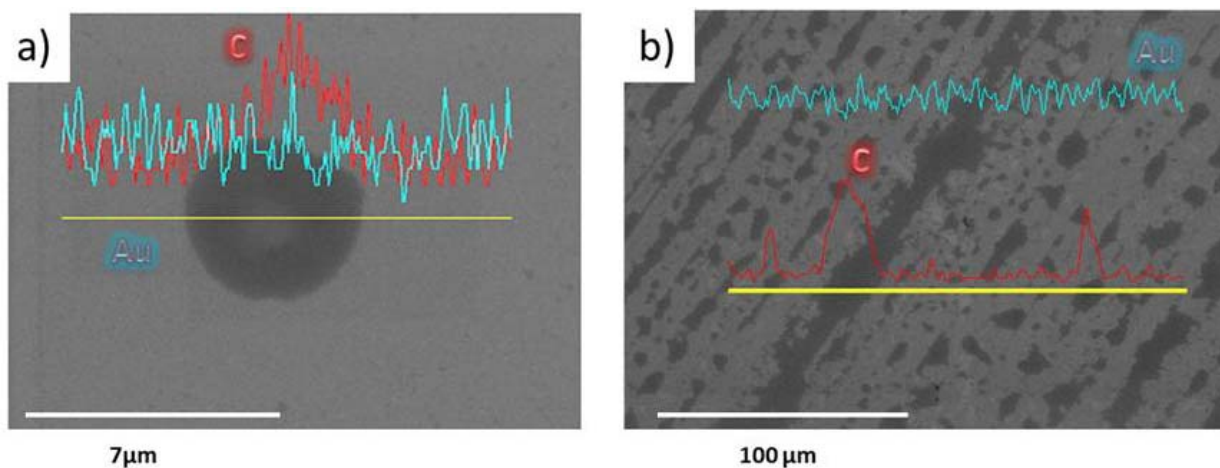
In order to confirm our assumption that the nanoparticles were indeed composed of PS (and no other chemical compositions at the surface), we used Raman spectroscopy. The Raman spectrum of the self-assembled nanoparticles, taken from the same area of the AFM mapping, clearly indicated that the particles were composed of PS (Figure 3). The main Raman peaks appeared at 1,006.1  $\text{cm}^{-1}$ , 1,035.1  $\text{cm}^{-1}$ , 2,901.6  $\text{cm}^{-1}$ , and 3,058.1  $\text{cm}^{-1}$  were attributed to C-C chain rocking,  $\text{CH}_2$  ring rocking in plane, asymmetric  $\text{CH}_2$  chain stretching, and CH ring stretching respectively. Those values are suitable for a typical PS Raman spectrum [37]. To further identify the absolute chemical



**Figure 2:** AFM image of the PS nanoparticles assembled on the surface (a), scale bar=4.7  $\mu\text{m}$ , and a height profile of the marked line (b).



**Figure 3:** Micro-Raman spectrum of PS nanoparticles assembled onto NDA-Au surface.



**Figure 4:** HR-SEM images combined with element line-scan of: a single PS nanoparticle (a), and assembled PS nanoparticles (b).

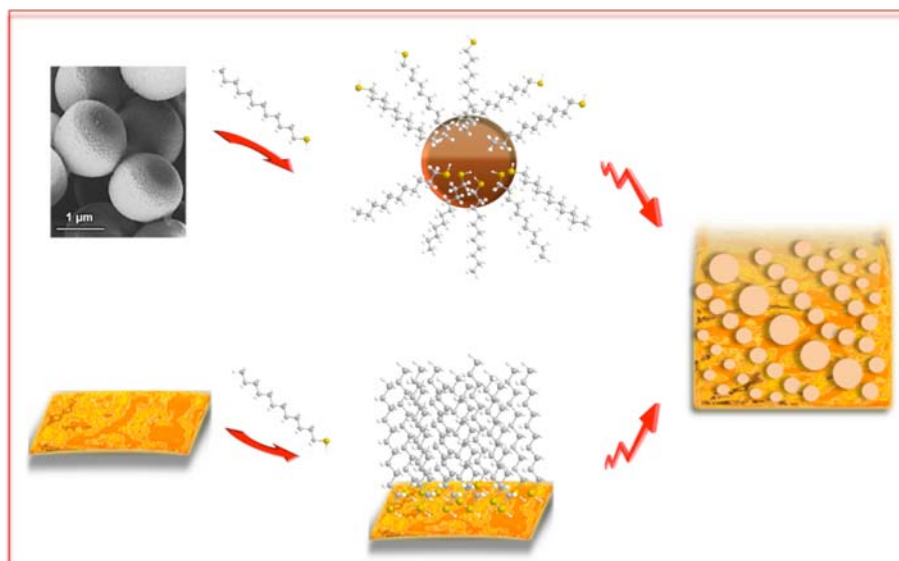
composition of the particles, EDS line-scan was incorporated with HR-SEM images of a single PS nanoparticle (Figure 4a), and self-assembled PS nanoparticles (Figure 4b). The EDS scan-line proved the presence of Au and C at the surface.

Bellow, we propose a possible mechanism, as schematically shown in Figure 5. The process started with the preparation of micro-size Au/PS Janus particles, and an ultrafast Au substrate (100 nm). Next, we performed SAMs of NDA on both the Au substrates and the Au/PS Janus particles. In the next stage, the Au/PS Janus particles were chemically adsorbed onto the NDA-Au surfaces due to hydrophobic molecular interactions. At that point, we could accomplish that the

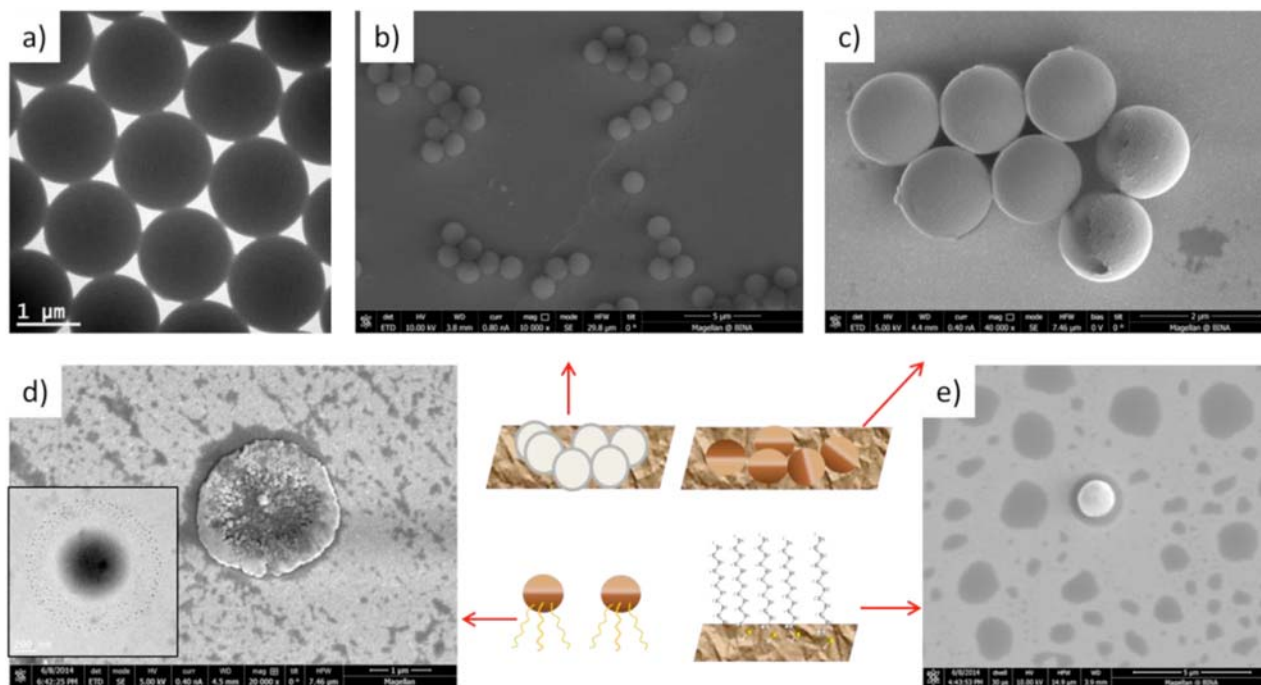
NDA gradually dissolved the Au/PS Janus particles into PS nanoparticle, and simultaneously directed them into ordered assemblies of PS nanoparticles. The use of the Au/PS Janus particles played a key role since the Au coating on half of the PS surface provided protection from a fast dissolution of the non-cross linked PS particles by NDA. Our mechanism for the preparation of ordered assemblies on a surfaces differs from those based on the growth of nanoparticles on a surface.

In order to confirm the proposed mechanism, we performed a few control experiments, schematically described in Figure 6. The initial PS micro-sized particles (shown in TEM image, Figure 6a) showed a





**Figure 5:** Scheme outlining the spontaneous arrangements of Au/PS Janus particles into PS nanoparticles onto NDA-Au surfaces.

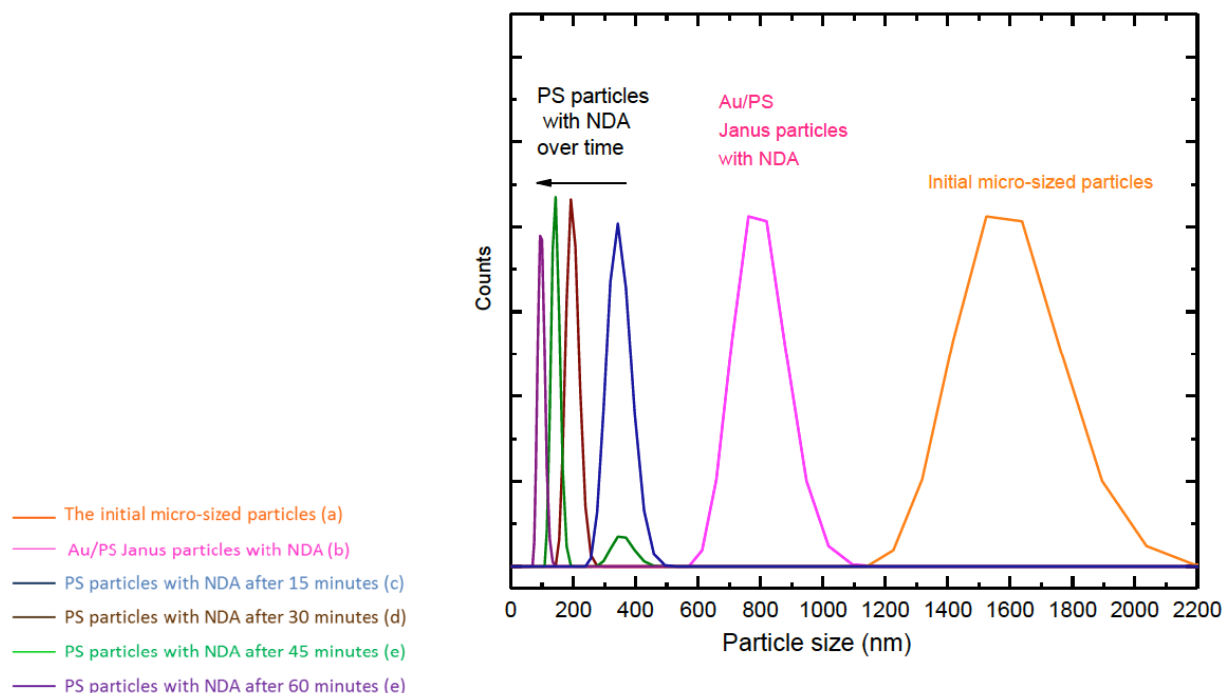


**Figure 6:** TEM image of the initial PS micro-sized particles (a), and SEM image of PS particles, no NDA(b); SEM image of Au/PS particles, no NDA (c); SEM image and TEM (inset) of Au/PS particles with NDA, no NDA on the Au substrate (d); and Au/PS particle dissolved by NDA on Au substrate (e). Center: drawings of the experiments.

non-specific ordering on Au surface in the absence of NDA (Figure 6b). Additionally, the Au/PS Janus particles without any NDA in the dispersion, neither on the Au substrate, yet demonstrated no arrangements (Figure 6c). Furthermore, when the NDA was bounded only to the Au/PS particles, a dissolution process was observed. However, no special assemblies were found (shown in SEM and TEM images, Figure 6d). Finally, Au/PS Janus particles showed no arrangement onto Au

substrate bounded with NDA (Figure 6e). The above experiments did not show any specific arrangements; therefore we concluded that the ordered assemblies appeared only when the NDA was bounded both to the Au/PS Janus particles and the Au surface.

In order to further demonstrate the dissolution mechanism of the non-cross linked PS particles by NDA, we performed DLS measurements of the



**Figure 7:** DLS measurements of; the initial particles (a); the Au/PS Janus particles with NDA (b); the PS particles after 15 minutes (c), 30 minutes (d), 45 minutes (e), and 60 minutes (f).

particles in the presence of NDA over time (Figure 7). The calculated size of the initial particles was  $1580 \text{ nm} \pm 400 \text{ nm}$  (Figure 7a), matching the diameter of the initial PS micro-sized particles (averaged size  $1.65 \text{ }\mu\text{m}$ ). The calculated size of Au/PS Janus particles in the presence of NDA was  $790 \text{ nm} \pm 250 \text{ nm}$  (Figure 7b). Their size remained stable over 60 minutes, indicating a high stability due to the Au coating. However, the DLS measurements of bare PS particles revealed that without the Au coating, a tremendous decrease in size over time in the presence of NDA occurred (Figure 7c-7f). Their size and size distributions were decreased from  $345 \text{ nm} \pm 150 \text{ nm}$  after 15 minutes (Figure 7c), through  $142 \text{ nm} \pm 53 \text{ nm}$  after 30 minutes (Figure 7d), and after 45 minutes two populations of  $356 \text{ nm} \pm 80 \text{ nm}$  and  $125 \text{ nm} \pm 67 \text{ nm}$  were observed (Figure 7e), and finally, after 60 minutes, a population of  $97 \text{ nm} \pm 42 \text{ nm}$  was measured (Figure 7f). We assume that in the self-assembly step, the Au/PS Janus particles were detached onto the Au surface mostly through the free PS surface of the Janus particle and not through the Au-coated surface. The hydrophobic PS surface interacted with the lipophilic chains of the NDA and attached the NDA-Au surface; this enabled the PS dissolution on the Au surface to produce the PS-NDA-Au interface. The dissolution has occurred simultaneously with the direction of the well-ordered NDA at the Au surface.

#### 4. CONCLUSIONS

In this work we report on a new method for the production of ordered self-assembled PS nanoparticles from Au/PS Janus particles onto NDA-Au surfaces, and propose a possible mechanism for the self-assembly process. This self-assembly method is relatively straight-forward, does not require any mechanical or physical special technique, occurs under ambient conditions, and free of organic solvents or toxic agents. This facile approach for producing a large-scale of self-assembled PS nanoparticles can be extended for advanced uses at the surface science.

#### ACKNOWLEDGEMENTS

The authors would like to thank Moshe Feldberg for the sputtering process, and to acknowledge Ido Fuchs and Merav Mualem for the HRSEM measurements, and Anya Muzikansky for the DLS measurements. Ortal Lidor-Shalev acknowledges the Bar-Ilan President's Ph.D. Scholarship Foundation. This research was supported by the Israel Science Foundation (ISF) (Grant No. 775/11).

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[http://dx.doi.org/10.1016/S0368-2048\(97\)00023-6](http://dx.doi.org/10.1016/S0368-2048(97)00023-6)

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Received on 21-09-2015

Accepted on 16-12-2015

Published on 12-01-2016

DOI: <http://dx.doi.org/10.6000/1929-5995.2015.04.04.5>