

The systematic tunability of nanoparticle dimensions through the controlled loading of surface-deposited diblock copolymer micelles

S Krishnamoorthy¹, R Pugin¹, C Hinderling¹, J Brugger² and H Heinzelmann¹

¹ Centre Suisse d'Electronique et de Microtechnique SA, Jaquet Droz 1, CH-2007 Neuchâtel, Switzerland

² Ecole Polytechnique Fédérale de Lausanne (EPFL), Laboratoire de Microsystèmes, CH-1015 Lausanne, Switzerland

E-mail: raphael.pugin@csem.ch

Received 18 December 2007, in final form 24 February 2008

Published 25 March 2008

Online at stacks.iop.org/Nano/19/175301

Abstract

The continuous tunability of iron oxide nanoparticle dimensions is demonstrated using the pH controlled loading of ferric nitrate from aqueous solution into polystyrene–block–polyacrylic acid reverse micelles deposited on a silicon substrate. Quasi-hexagonally ordered two-dimensional arrays of iron oxide nanoparticles with a systematic tunability of particle heights in the sub-10 nm regime and a constant periodicity are obtained and characterized with atomic force microscopy and x-ray photoelectron spectroscopy.

1. Introduction

The novel physical and chemical properties exhibited by nanostructures and the promise they offer for device miniaturization has attracted widespread attention in recent years [1, 2]. The properties of the nanostructures are size- and shape-dependent and hence it is important to be able to reproducibly create these structures with desired specifications. Surface-supported nanostructures are particularly sought-after for integration into on-chip devices such as sensors, display systems, IC chips and memory devices. Applications that require control over surface wettability [3], influence on the behavior of cells [4] and biomolecules [5] on surfaces also benefit from the use of nanostructured interfaces. Nanopatterning surfaces with topographic, chemical or biochemical contrast in the sub-100 nm regime have been shown earlier using self-organization of colloidal microspheres [6, 7], dendrimers [8], proteins [9] and microphase-separated copolymer thin films [10–12] or copolymer micelles [13–15]. Copolymers are best suited for facile creation of nanostructures down to sub-10 nm dimensions with narrow dispersion (typically <15%), high density (\sim Terabit inch⁻²) and excellent homogeneity over

large areas (full-wafer level). Creating nanostructures using copolymer micelles deposited from the solution phase offer an attractive alternative to phase-separated thin films, as most benefits of the latter can be achieved from the use of micellar films even in the as-coated form, without the need for elaborate processing steps. Formation of metal/metal oxide nanoparticle arrays using copolymer reverse micelle arrays has been shown earlier through loading of the micellar cores with a metal precursor, followed by an oxidation or reduction step to create the nanoparticles [16, 17]. Tunability of the resulting particle dimensions has been achieved mainly by varying the concentration of the metal salt in the solution phase during the loading step [18–21]. This process, however, suffers from the limitation that the nanoparticles of only those materials are obtainable whose salts are soluble in organic solvents such as toluene or xylene that are employed to prepare copolymer reverse micelles. In addition, loading the micelles before deposition is likely to interfere with the periodicity of the micelle arrays formed thereby, also influencing the resulting nanoparticle array periodicity. Boontongkong *et al* has reported the approach of depositing polystyrene–block–polyacrylic acid (PS-b-PAA) reverse micelle thin films on substrates followed by the exposure of the dried thin films to

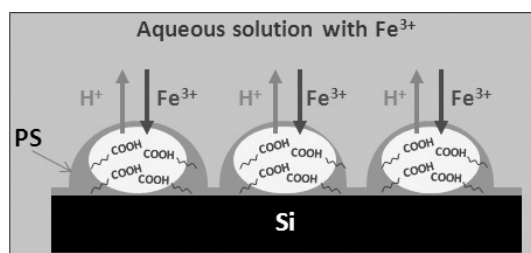


Figure 1. Schematic showing the exchange equilibrium between ferric ions in an aqueous medium with protons of carboxy functional groups within cores of the PS-b-PAA reverse micelle monolayer.

an aqueous salt solution to load the core with metal ions [16]. This approach is highly advantageous, considering that the deposition and loading steps are well separated. Besides, the use of aqueous solutions of metal salts opens up wide ranging possibilities for the choice of materials usable. In this paper, we have therefore employed this approach to load ferric ions into PS-b-PAA reverse micelle arrays deposited on silicon surface, and demonstrate control over the degree of loading by controlling the ion exchange equilibrium (figure 1). This approach yields iron oxide nanoparticle arrays with particle dimensions systematically tunable in steps of ~ 2 nm in the sub-10 nm regime.

2. Copolymer reverse micelle arrays

PS-b-PAA ($16500\text{-}b\text{-}4500$ g mol⁻¹) with a PDI of 1.05 was purchased from Polymer Source Inc. (Montreal, Canada). 0.5% (w/w) of the solution of the polymer was prepared in toluene. The micelle solution was prepared with minor modifications to the already reported procedure [16]. The solution which is initially cloudy was annealed in a sealed tube for an hour at 140 °C to obtain a clear solution containing spherical micelles. Light scattering measurements were carried out on the micelle solution using the ALV autocorrelator set-up using a red laser of $\lambda = 633$ nm, with capabilities for simultaneous dynamic light scattering (DLS) and static light scattering (SLS) measurements. The data were acquired between 30° and 150° angles in 10° steps. Light scattering measurements indicate an aggregation number of 284 and a hydrodynamic radius of 29 nm for the reverse micelles. Freshly piranha treated silicon substrates were silanized with octadecyl trichlorosilane by vapor phase exposure for 3 h followed by washing in n-hexane, ethanol and millipore water. The micelles were deposited on the silanized silicon substrate by spin-coating at 5000 rpm. The silanization of the substrate prior to micelle deposition was necessary to suppress the lifting off of the thin film from the substrate, when dipped in salt solutions for several hours. The micellar thin films on the surface were characterized using atomic force microscopy (AFM) in tapping mode. The AFM measurements were performed with a Veeco Dimension 3100 instrument and controlled by the Nanoscope software to assess the topography and film thickness (by measuring across a manual scratch).

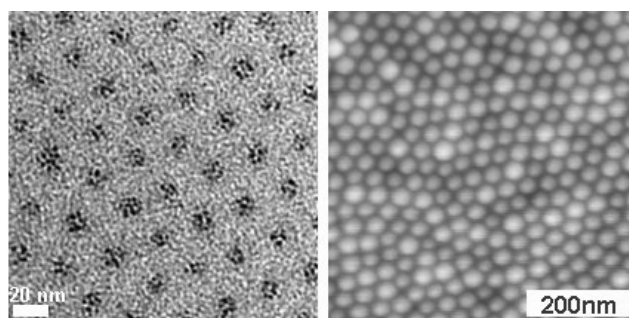


Figure 2. (Left): TEM image of PS-b-PAA micelles loaded and stained with CdCl₂. (Right): tapping mode AFM image of a monolayer of PS-b-PAA micelles on a silicon surface (Z scale = 30 nm).

3. Tunable iron oxide nanoparticle arrays

Monolayer micellar films displayed a topography of quasi-hexagonally arranged bumps with a height of 4 nm with a mean interparticle distance of 27 nm (figure 2 right). The total thickness of the micellar film as determined by AFM was 15 nm. Transmission electron microscopy (TEM) (Philips CM200) was performed on the micelles that were drop-coated onto a carbon-coated copper grid and stained with CdCl₂ (50 mg ml⁻¹) for 1 min. The core diameter of the micelles was estimated to be 10 nm from the TEM measurements (figure 2 left).

0.01 M solutions of Fe(NO₃)₃ in aqueous HNO₃ solutions of molarities of 1, 0.8, 0.5, 0.3, 0.1, 0.01 and 0 were used for loading (we calculate the respective pH values of the HNO₃ solutions to be 0, 0.095, 0.30, 0.52, 0.99, 1.87 and 2.33). To load the micellar cores with ferric ions, the micelle-coated substrates were dipped in the aqueous solution of ferric nitrate (loading solution) for 12 h followed by rinsing with millipore water. When dipped in ferric salt solution, the Fe³⁺ ions in the medium exchange with the H⁺ of the COOH functional groups in the PAA core. In order to maintain charge neutrality, the binding of each ferric ion within the micellar core requires expulsion of three protons out of the PAA core and into the medium (figure 1). If the concentration of H⁺ ions in the medium is increased, it influences the Fe³⁺/H⁺ ion exchange equilibrium by suppressing the dissociation of COOH groups. Higher acidity of the loading salt solution thus results in less ion exchange and hence less metal ion loading. This enabled us to systematically vary the quantity of ferric ions loaded within the core by varying the pH of the loading solution. The subsequent oxygen plasma exposure (30 W, 50 mT, 3 min using Oxford Plasmalab80) of the salt-loaded micelles removes all polymer and results in the formation of iron oxide nanoparticles, as confirmed by the XPS measurements on the particle arrays (figure 3(b)). XPS measurements indicate the presence of iron in both +2 and +3 oxidation states, indicating a mixture of oxides. The size of the resulting nanoparticles are a function of the salt loaded within the micelles. The sizes were compared by determining the particle heights rather than diameters, since the height measurements are free from AFM tip convolution effects.

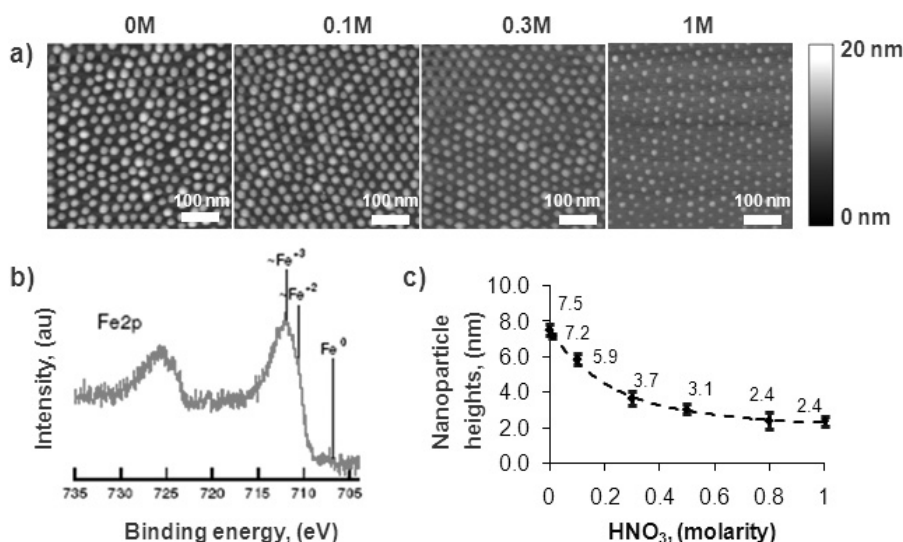


Figure 3. (a) Tapping mode AFM images showing a decrease in iron oxide nanoparticle dimensions with an increase in acidity of the loading solution. The concentration of HNO₃ used is indicated. The scale bars indicate 100 nm. (b) XPS characterization of the nanoparticle arrays showing iron in +3 and +2 oxidation states. (c) Plot showing a systematic decrease in nanoparticle heights as measured using tapping mode AFM, as a function of nitric acid concentration in the loading solution.

4. Results and discussion

The nanoparticles were found to have a mean height of 7.5 (± 0.3) nm and dispersity of 14.6%, when an aqueous solution is used for loading. With the addition of HNO₃ in the loading solution, the resulting nanoparticle sizes decrease as a function of HNO₃ concentration. The mean particle heights systematically decrease from 7.5 nm to 2.4 nm with a [HNO₃] change from 0.01 to 1 M. The particle arrays were prepared on a SiO₂-coated TEM grid to analyze the particles after oxygen plasma. The particles were found to be non-crystalline. The homogeneity of the nanoparticle arrays formed on the Si substrate was confirmed by SEM analysis (not shown).

The maximum size of the nanoparticles that can be obtained depends on the concentration of the functional groups within the micellar core. This can be calculated from the value of the aggregation number and the molecular weight of the PAA block. Assuming that all the carboxylic acid groups take part in loading, and assuming the particle composition and density correspond to that of α -Fe₂O₃, the resulting nanoparticle dimension of 6.6 nm diameter can be arrived at, assuming a spherical geometry. This value is closer to, but smaller than, what we observe as particle heights in the AFM. The apparent discrepancy between the calculated and observed values could stem from the values of density used and the assumption on sphericity of the particles.

5. Conclusions

We have thus demonstrated a simple and efficient means of controlling the dimensions of iron oxide nanoparticle arrays in a systematic way, by controlling the equilibrium of metal ion binding to the functional core of copolymer reverse micelles deposited on the surface. The particle dimensions were shown to be tunable in the sub-10 nm regime while keeping array

periodicities constant. The approach described can easily be extendible to obtain size-tunable particle arrays of a variety of other metal oxide and metal nanoparticles. The iron oxide nanoparticles are known catalysts for growing carbon nanotubes (CNT), and the tunability of the catalyst particle dimensions as achieved in this work can be exploited to grow CNTs of tunable diameters. Further work in this direction is underway.

Acknowledgments

The work described in this paper was supported by the National Center of Competence in Research (NCCR) in nanoscale science of the Swiss National Science Foundation for Scientific Research. We thank them for their support. We thank Dr Corinne Vebert and Olivier Casse, Department of Chemistry of the University of Basel for their help with the light scattering measurements and fruitful discussions. We thank Dr Teresa de los Arcos and Michael Büttner, Department of Physics of the University of Basel for their help with the XPS measurements.

References

- [1] Rao C N R, Kulkarni G U, Thomas P J and Edwards P P 2002 *Chem. Eur. J.* **8** 29
- [2] Shipway A N, Katz E and Willner I 2000 *ChemPhysChem* **1** 18
- [3] Patankar N A 2004 *Langmuir* **20** 8209
- [4] Spatz J P 2004 *Nanobiotechnology* **5** 3
- [5] Agheli H, Malmstrom J, Larsson E M, Textor M and Sutherland D S 2006 *Nano Lett.* **6** 1165
- [6] Wood M A 2007 *J. R. Soc. Interface* **4** 1
- [7] Yang S M, Jang S G, Choi D G, Kim S and Yu H K 2006 *Small* **2** 458
- [8] Frechet J M J 2003 *J. Polym. Sci. A* **41** 3713
- [9] Kubota T 2004 *Appl. Phys. Lett.* **84** 1555
- [10] Hamley I W 2003 *Nanotechnology* **14** R39–R54
- [11] Mansky P, Harrison C K, Chaikin P M, Register R A and Yao N 1996 *Appl. Phys. Lett.* **68** 2586

- [12] Park M, Harrison C, Chaikin P M, Register R A and Adamson D H 1997 *Science* **276** 1401
- [13] Shimomura M and Sawadaishi T 2001 *Curr. Opin. Colloid Interface Sci.* **6** 11
- [14] Krishnamoorthy S, Pugin R, Heinzelmann H, Brugger J and Hinderling C 2006 *Adv. Funct. Mater.* **16** 1469
- [15] Krishnamoorthy S, Pugin R, Brugger J, Heinzelmann H, Hoogerwerf A C and Hinderling C 2006 *Langmuir* **22** 3450
- [16] Boontongkong Y and Cohen R E 2002 *Macromolecules* **35** 3647
- [17] Spatz J P, Roescher A and Moller M 1996 *Adv. Mater.* **8** 337
- [18] Spatz J P *et al* 2000 *Langmuir* **16** 407
- [19] Kastle G *et al* 2003 *Adv. Funct. Mater.* **13** 853
- [20] Yun S H, Sohn B H, Jung J C, Zin W C, Lee J K and Song O 2005 *Langmuir* **21** 6548
- [21] Fu Q, Huang S M and Liu J 2004 *J. Phys. Chem. B* **108** 6124