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Effect of gold nanoparticle hydrophobicity on thermally induced color change of PNIPAM brush/gold nanoparticle hybrids

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ABSTRACT

This paper addresses the relation between gold nanoparticle (AuNP) distribution in thermoresponsive polymer brushes and the thermally induced color change of the polymer brush/AuNP hybrids. Therefore, we report on the effect of AuNP surface functionalization on the structure and optical response of the nanoparticles in thermoresponsive poly(*N*- isopropylacrylamide) (PNIPAM) brushes. Two different types of gold nanoparticles are attached to the PNIPAM brushes: (1) AuNPs that are coated with citrate anions (AuNP-citrate), and (2) AuNPs stabilized with 12-mercaptododecanoic acid ligands (AuNP-MDA). Neutron reflectivity (NR) measurements indicate that the spatial structure of the hybrid depends on the particle type. A strong increase in thickness is observed after attachment of AuNP-citrate; this is not the case for AuNP-MDA. The thermoinduced color change of the PNIPAM/AuNP hybrids depends strongly on the particle type. While a red-shift of the surface plasmon band occurs in case of AuNP-citrate, a blue-shift is found for AuNP-MDA when the temperature is increased above the PNIPAM's volume phase transition temperature. This blue-shift vanishes after a certain number of heating/cooling cycles, indicating a rearrangement of the AuNPs in the brush. The different behavior of AuNP-citrate as compared to AuNP-MDA can be explained by the hydrophobic nature of the 12-mercaptododecanoic acid ligands.

1. Introduction

Polymer chains end-grafted to a substrate, known as polymer brushes, can be used as nanosensors by embedding metal nanoparticles into the polymer matrix [1,2]. Using nanoparticles that exhibit the surface plasmon resonance (SPR) phenomenon allows detecting changes in the surrounding environment by means of color changes [3,4]. The detected property usually varies depending on the chemical nature of the polymer matrix. There are several examples where pH-responsive brushes were employed as templates for the attachment of gold nanoparticles; plasmon band shifts occurred when the pH of the surrounding environment was changed [5–8]. However, more recently it was reported that not all stimuli-responsive brushes preserve their sensitivity to external stimuli after incubation with gold nanoparticles [9]. A prominent temperature-sensitive polymer is poly(*N*-isopropylacrylamide) (PNIPAM) which exhibits a lower critical solution temperature (LCST) at ~32 °C in aqueous solution. Thermosensitive optical sensors of end-grafted PNIPAM chains have been studied to some extent in the past [10–12]. As demonstrated by Mitsuishi and co-workers [10], the plasmon band of citrate-capped gold particles of 40 nm diameter attached to PNIPAM brushes of around 40 nm ambient height shifted from 540 to 546 nm when the temperature increased above the LCST of PNIPAM. A larger plasmon shift was found by Gupta and co-workers [11] where smaller gold spheres (5–6 nm diameter) functionalized with 11-mercaptoundecanoic acid (MUA) were attached to PNIPAM chains and showed a plasmon shift of ~12 nm upon increasing the temperature to 40 °C. In their work, they employed PNIPAM brushes which were grown by the *grafting to* approach and exhibited a grafting density of 0.15 nm^{-2}. The PNIPAM brushes in this work are grown by the

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grafting from approach which yields to much higher grafting densities. A typical value of brushes grown by surface-initiated atom transfer radical polymerization (SI-ATRP) is 0.5 nm^{-2}, a value determined by cleaving polymer brushes from the surface [13].

The optical response of such brush/particle hybrids depends on the concentration and distance of the particles inside the brush. To enhance the optical response of the system, the particles should penetrate the brush matrix to form a 3D assembly. Very low particle loading may result in non-sufficient plasmon coupling; very high particle loading may result in irreversible formation of aggregates. Strategies to tune the proximity of the particles inside a polymer brush matrix include variations of brush grafting density [14,15] or brush molecular weight [16,17]. This is an active approach to tune the particle assembly as it requires variations of the brush properties. In this work, we will elaborate whether the particle assembly in brushes can also be controlled by the particle properties, i.e. the hydrophobicity of the AuNPs. This can be achieved by using AuNPs with different coatings.

In this paper, two different gold particle types are impregnated into thermosensitive poly(*N*-isopropylacrylamide (PNIPAM) brushes, hydrophilic citrate-coated gold nanoparticles (AuNP-citrate) and more hydrophobic 12-mercaptododecanoic acid (MDA)-coated gold nanoparticles (AuNP-MDA) of ~4 nm diameter. AuNP-citrate are dispersed in water; AuNP-MDA cannot be dispersed in water and are dispersed in toluene. The thermoresponsive brush matrix was chosen because temperature is an easy parameter to vary; this allows a pretty straightforward investigation of such brush/nanoparticle hybrids (structure and optical properties) in liquid environment. This is an important aspect since sensors work in liquid environment.

The particle surface functionalization determines the choice of solvent (water, toluene) and with that, the brush conformation during particle attachment. Hydrophilic PNIPAM brushes will be more swollen in water as compared to toluene [18]. This will affect the structure of the resulting hybrid and, in turn, have an impact on the optical response of the system. For both particle types, the particle attachment is driven by hydrogen bonding between the amide groups of the NIPAM units and the respective coating of the gold particles (via carboxylic acid groups). The uptake of small (~3.5 nm) citrate-coated AuNPs into PNIPAM brushes was previously investigated by Bhat and co-workers [15]. In their work, it was found that the uptake of AuNP into the PNIPAM brush matrix depended on the grafting density; the highest AuNP loading occurred for intermediate grafting densities. However, the spatial distribution of AuNP-citrate in the PNIPAM brush matrix is still unclear. However, X-ray photoelectron spectroscopy (XPS) experiments of poly(acrylamide) (PAAm) brushes with impregnated AuNP-citrate (~3.5 nm) suggested that the small particles were able to penetrate into PAAm brushes of ~10 nm thickness but did not penetrate into thinner brushes (~5 nm thickness) [19].

In this work, neutron reflectivity (NR) will be used to study the structure of hybrids made of PNIPAM and the two different particle types, namely PNIPAM/AuNP-citrate and PNIPAM/AuNP-MDA. In the past, NR was employed by Yim and co-workers to study the conformational change of surface grafted PNIPAM brushes upon increasing the temperature above PNIPAM's LCST [20–22]. They obtained a single box profile with low roughness for collapsed PNIPAM brushes above the LCST. Below the LCST, a single box profile with roughness, or a parabolic profile with exponential tail could not be used to fit the NR data. Therefore, the authors employed a bilayer profile to describe the swollen structure of PNIPAM brushes [21,22]. To describe the swollen structure of surface-grafted PNIPAM brushes more precisely, we employ a multi step-like fitting model which accounts for the polydispersity of the grafted polymer chains and does not require roughness as a fitting parameter. Further, UV/vis spectroscopy will be carried out to study the color change of PNIPAM/AuNP-citrate and PNIPAM/AuNP-MDA upon increasing the temperature above the phase transition temperature of PNIPAM.

Our findings suggest that the structure of the PNIPAM/AuNP hybrids in liquid environment depends strongly on the particle type. Whereas a strong collapse of PNIPAM/AuNP occurs at temperatures above PNIPAM's LCST when citrate-coated AuNPs are immobilized in the brush matrix, the collapse is less distinct in case of MDA-coated AuNPs. The largest difference in behavior is found when investigating the color change associated with an increase of the temperature above PNIPAM's LCST. In case of citrate-coated AuNPs, a red shift of the gold surface plasmon (SP) band is obtained, mostly caused by a decrease in interparticle distance in the collapsed brush. In case of the MDA-coated AuNPs, we observe a blue shift which is caused by the better dispersion of the hydrophobic particles in the collapsed brush matrix leading to an average increase in interparticle distance. This work shows that the optical properties of such hybrid systems can be manipulated by tuning the properties of the brush itself (swelling/shrinking) but also by tuning the particle properties (hydrophilic/hydrophobic). The ability to control assembly of metallic nanoparticles in stimuli-responsive polymer templates provides a platform for obtaining defined colloidal nanostructures, which are used in the development of nanophotonic devices, switches, resonant light scatterers, waveguides, and sensors [3,23]. In this work, we employed a thermosensitive polymer matrix as a model system to study the effect of particle assembly on the color change. Our findings can be translated into other stimuli-responsive systems and one could think of a variety of possible nanosensors capable of detecting changes in pH value [5–8,14], solvent [24], or environmental pollutants such as lead cations [25]. In addition, properties such as responsiveness to external stimuli, high chemical and mechanical stability, biocompatibility, tunable optical properties, and tunable wettability of such hybrid nanosystems makes them ideal candidates for applications in molecular engineering, medical diagnostics, catalysis, information storage and nanotechnology [1].

2. Experimental part

2.1. Materials

N-isopropylacrylamide (NIPAM), trimethoxy(propyl)silane (TMS), *N*,*N*,*N*',*N*'',*N*''- Pentamethyldiethylenetriamine (PMDETA), copper(I)chloride (CuCl), sodium borohydride ($NaBH_4$), gold(III) chloro trihydrate ($HAuCl \times 4\ 3\ H_2O$), sodium citrate dihydrate, tetraoctylammonium bromide (TOAB), 12-mercaptododecanoic acid (MDA), ethanol (EtOH), toluene, and methanol (MeOH) were purchased from Sigma–Aldrich and used without further purification. Silicon substrates (<100> orientation, Boron/p-doped, polished) were purchased from Microchemicals GmbH (Ulm, Germany) and cut into pieces of 1 cm × 2 cm and were used for ellipsometry measurements. Glass substrates (Fused Silica JG52, polished) with dimensions of 1 cm × 2 cm were purchased from MicroChemicals GmbH and were used for UV/vis spectroscopic measurements. For neutron reflectivity measurements, Silicon blocks with dimensions of 5 cm × 8 cm × 1.5 cm were used.

2.2. Synthesis

2.2.1. PNIPAM brushes

Before synthesis, the substrates (silica or glass) were rinsed with methanol, sonicated in methanol for ~15 min, cleaned with methanol and dried under a stream of nitrogen. A self-assembled monolayer (SAM) of 2-bromo-2-methyl-*N*-(3-(triethoxysilyl)