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Nanoparticles selectively immobilized onto large arrays of gold micro and nanostructures through surface chemical functionalizations

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ABSTRACT

Latex nanoparticles (100 nm and 200 nm diameter) were precisely located onto the gold regions of micro and nanopatterned gold/silica substrates through surface chemical functionalizations. The gold patterns were selectively functionalized with alkylthiols bearing biotin or amine headgroups. This selective functionalization allowed the trapping of streptavidin- or carboxy-functionalized latex nanoparticles onto the gold structures with very little non-specific adsorption onto the surrounding silica. Quantitative data of nanoparticle capture on gold and silica, obtained through SEM image analysis, showed a one to two order of magnitude increase on gold with a similar low coverage on silica (non-specific adsorption) thanks to chemical functionalizations. Single nanoparticles were captured at the gap of dimer gold nanostructures.

1. Introduction

Finding reliable and simple methods for the precise self-assembly of colloids onto different regions of a patterned surface is a major current issue in nanofabrication [1–6]. Solving this issue could bridge the gap between top-down fabrication processes such as lithography which allows the creation of large arrays of well-defined nanostructures on a surface (e.g., plasmonic nanoantennas or electrodes) and bottom-up built nano-objects with unique physicochemical properties (e.g., fluorescent nanoparticles or silicon nanowires) [7,8]. Surface chemical functionalization can be used to tune the short-range attractive or repulsive interaction between colloidal particles and a planar surface and thus allow the selective trapping of colloids onto precise regions of a heterogeneous substrate. Three major schemes for colloid trapping through surface functionalization can be seen in the literature, based on: (1) electrostatic forces [9–16], (2) covalent bonding [9,17–22], and (3) bio-affinity such as nucleic acids hybridization [16,23–25] or biotin/avidin interactions [25,26]. One of the major challenges in this field is to achieve *parallel* capture of *single* (or few) particle(s) on an *array* of pre-defined nanometric regions of a surface (see Fig. 1).

To the best of our knowledge, only few of the above-mentioned references have achieved trapping of individual nanoparticles on nanometric regions [10,13,16,23]. Among them, the work of Bach and co-workers [16,23] uses pre-defined metallic nanostructures on a dielectric surface as trapping sites. The authors use nucleic acid hybridization to bind functionalized gold colloids onto gold nano-regions on a silica substrate. In this paper we demonstrate selective trapping of latex nanoparticles on gold micro and nanopatterns on a silica substrate through surface chemical functionalization with alkylthiols. Based on the thiols' headgroup, streptavidin- and carboxy-functionalized latex nanoparticles are trapped onto the gold regions by biotin/streptavidin biorecognition or by electrostatic bonds. Individual nanoparticles have been electrostatically trapped on dimer gold nanostructures envisioned to work as plasmonic nano-antennas. The use of latex nanoparticles (instead of metallic colloids [10,13,16,23]) enables an easy loading with different materials that can confer different properties to the nanoparticles, such as fluorescence at different wavelengths or magnetic properties. Such individual and parallel trapping of latex nanobeads has, to the best of our knowledge, never been shown before. Furthermore, the electrostatic-based trapping scheme represents a very easy and versatile method that can be applied to

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different materials which makes these results very promising for a wide range of applications.

2. Materials and methods

2.1. Substrate patterning

A silica thin film (100 nm) was sputtered onto clean silicon wafers. UV-lithography was used to define different patterns (lines, squares) with typical dimensions ranging from 2 to 100 μm and e-beam lithography was used to define large arrays of dimer nanostructures with typical dimensions around 100 nm, with a pitch of 5 μm. Chromium (3 nm) and gold (45 nm) were deposited by e-beam evaporation. After lift-off, the samples were cleaned by oxygen plasma to ensure that no residual resist remained on the surface. On parallel, plain gold films (same thin films as above but no lithography) were deposited to study the functionalization by polarization-modulation infrared reflection absorbtion spectroscopy (PM-IRRAS).

2.2. Gold functionalization

11-mercapto-1-undecylamine (MUAM) 99% and ethanol 99.8% were purchased from Sigma–Aldrich. HS-$(CH_2)_{11}$–NH–C(O)-Biotin 95% (MU-Biot) was purchased from ProChimia. Samples were immersed in a previously degassed 1 mM ethanolic solution of thiols (MUAM or MU-Biot) for 4 h at room temperature and then rinsed 2×5 min in fresh ethanol under sonication to remove potentially adsorbed multilayers, followed by a 5 min rinse in ultrapure water and then dried under nitrogen flow.

2.3. Colloid deposition

Streptavidin-functionalized magnetic latex particles (200 nm diameter, 5 mg/ml solid content, Bio Adem-Beads Streptavidin Plus) were purchased from Ademtech. 200 μl of bead solution were dissolved into 2 ml ultrapure water and washed twice by magnetic separation, supernatant removal and refilling with fresh ultrapure water. Eventually, the beads were dissolved into 2 ml immobilisation buffer 1X (Ademtech) in an centrifuge tube containing the sample surface.

Fluorescent carboxylatex particles (100 nm diameter, 2% solids, product code: F8799) were purchased from Life Technologies. The fluorescence properties were not used in the present work. 200 μl of bead solution were dissolved into 2 ml of PBS-1X adjusted to pH = 7.4, in a centrifuge tube containing the sample surface. The millimetric sample was maintained vertically in the centrifuge tube fully immersed in the bead solution without agitation at room temperature. No sedimentation of the colloidal dispersions was observed overnight.

In both cases the functionalized samples were immersed into the bead solution overnight and then rinsed twice with ultrapure water and dried under nitrogen. Three different samples were prepared for each bead solution with the same procedure. A reference (non functionalized) sample was also immersed in a solution of streptavidin-functionalized particles overnight and rinsed in the same way.

2.4. PM-IRRAS characterization

For evaluation of the different alkanethiolate SAMs on plain gold substrates by polarization-modulation infrared reflection absorbtion spectroscopy, we used a Nicolet 6700 FTIR spectrometer from Thermo Scientific© coupled to a Hinds Instrument© PEM-100 ZnSe photoelastic modulator driven at 50 kHz (polarization switch from p to s at 100 kHz). The acquisition and spectra analysis parameters, as well as theoretical elements about PM-IRRAS have been detailed elsewhere [27–29].

2.5. SEM image acquisition and analysis

SEM images were acquired with a Mira3 SEM from TESCAN at 5 kV acceleration tension with a detection of secondary electrons. These images were analyzed by ImageJ software. After binarization with appropriate threshold values manually set for each image and despeckle filtering, colloids and background surface appear with opposite values (black vs white or viceversa). It is thus easy to compute the percentage of gold and silica surface covered by colloids simply by computing the percentage of black or white pixels. See Fig. 3 for an example.

3. Results and discussion

3.1. Gold functionalization

Amino- and biotin-functionalized plain gold substrates were characterized by PM-IRRAS. The surface spectra showed characteristic peaks of MUAM and MU-Biot: in both cases, the main vibration modes for the undecyl chain can be seen at ca. 2922 cm^{-1} $\left(\nu_{CH_2}^{assym}\right)$, 2850 cm^{-1} $\left(\nu_{CH_2}^{sym}\right)$ and 1460 cm^{-1} (δ_{CH_2}). Furthermore, the position of the $\nu_{CH_2}^{assym}$ indicates the close-packing of the alkyl chains in the SAMs [29–33]. MUAM (Fig. 2, top spectrum) shows

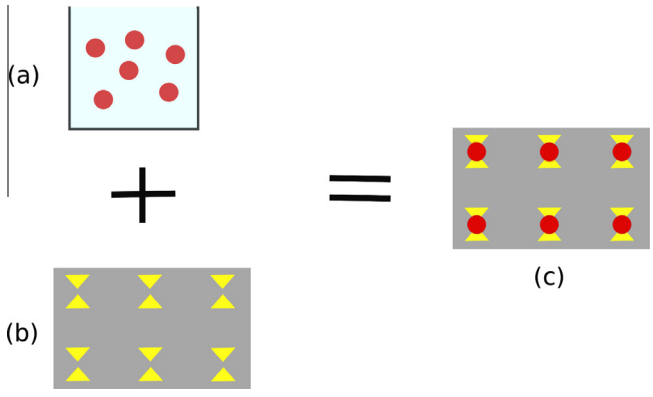

Fig. 1. Schematic representation of the precise localization of individual nanoparticles (c) from a colloidal dispersion (a) onto predefined nanometric regions on a substrate (b).

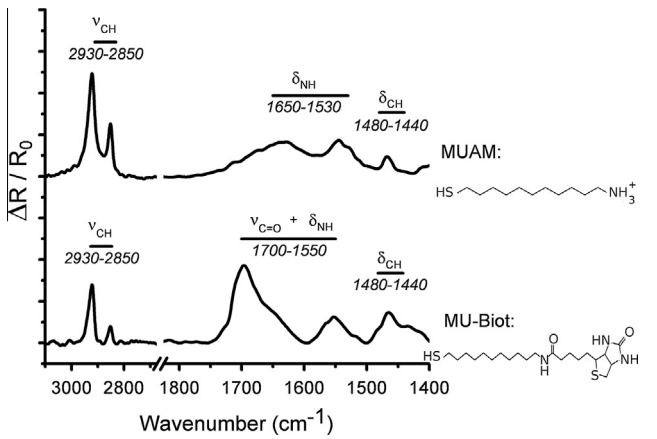

Fig. 2. PM-IRRAS spectra of gold surfaces functionalized with MUAM and MU-Biot.