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Assembling, locating, grafting and actuating permanent filaments for validation of Polarimetric Surface Plasmon Resonance Imaging system

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Abstract

We present a simple method combining magnetic field and micro or nano particles for assembling, locating and grafting permanent filaments onto various supports (homogeneous glass, gold surface or mixed gold/glass support). The actuation of these filaments by a magnetic field was used to validate a dynamical Surface Plasmon Resonance Imaging sensor (SPRI) capable to dynamically characterize anisotropy from the mean orientation of the surface-bound assemblies.

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1. Introduction

In recent year, the interest for magnetic particles and their manipulation by a magnetic field has increased. The study of the self-assembling ability of magnetic particles into filaments when subjected to an external magnetic field has allowed developing a new field called “macrocolloidal chemistry”. When the external magnetic field is removed, the chains disintegrate due to thermal motion. Permanently linked particle chains have been created using linker molecules which covalently bind particles together under magnetic field and make the filaments irreversible after magnetic field removal. These permanent particle

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chains could be addressed to specific area of a support. Permanent magnetic filaments have been made from micro (1mm) and nano (200 nm) activated beads under magnetic field and used in order to prove that a Polarimetric Surface Plasmon Resonance Imaging (P-SPRI) system is sensitive to the anisotropy of nano-objects.

Nomenclature

P-SPRI system Polarimetric Surface Plasmon Resonance Imaging system

ΔR Reflectivity difference

SEM Scanning Electronic Microscope

2. Results

2.1. Localization of permanent filaments

A simple method combining magnetic field and microparticles has been designed for assembling, locating and grafting permanent microfilaments onto homogeneous support by our team [1] or on mixed glass/gold support. The filaments could also be actuated by an external magnetic field while keeping their stable anchorage on the surface: their orientation is tunable in real time within a 2π solid angle.

In-situ permanent filaments orthogonal to a support were implemented by assembling magnetic carboxylate particles under magnetic field using the following methodology. Activated magnetic particles were deposited in solution on an activated solid support. By applying a magnetic field orthogonal to the surface, the magnetic particles self-assembled in chains. PEG-diamine chains were then used to covalently bind two particles or a particle and the support. Two methods of addressing (Fig. 1) were tested:

- Filaments were located on precise support zones by using metallic tips concentrating locally the magnetic field.
- Filaments were located on gold spots by using a selective functionalization on mixed support.

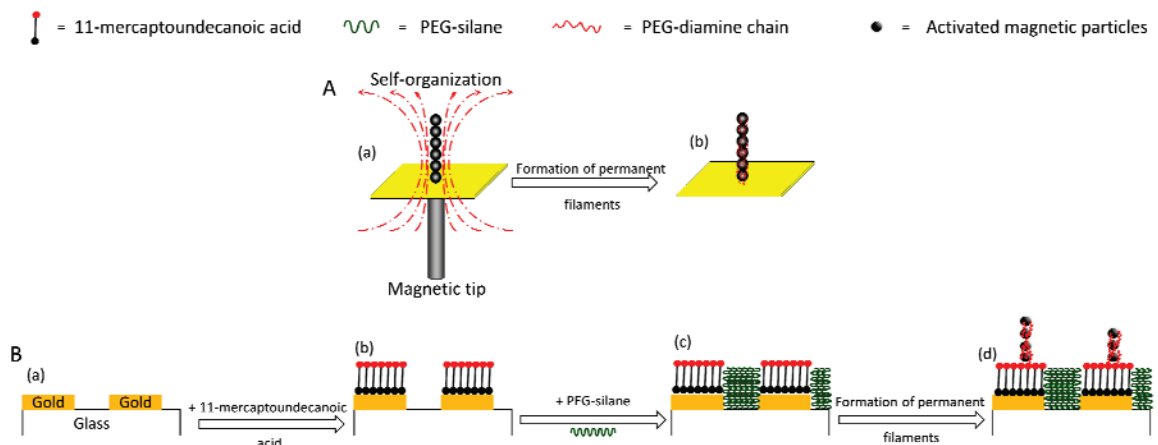


Fig. 1: A- Localization of filaments by magnetic tips. (a) Magnetic field is located on an activated gold surface using metallic tip. Activated magnetic particle self-organized following magnetic field line. (b) Formation of permanent filaments grafted on the gold surface using PEG-diamine chain. B- Selective functionalization mix support. (a) Gold deposition by thermal evaporation. (b) Self-assembled monolayer (SAM) formation of alkanethiols. (c) Glass protection by PEG-silane layer. (d) Formation of permanent filaments using PEG-diamine chain.

In the first method, the magnetic field applied through metallic tips leads to a high concentration of magnetic particles near the surface on top of the tips. Since beads were only present on those zones, no polymerization occurred on the rest of the support. In the second method, a selective functionalization of a mixed support (gold + glass) is done. Gold spots were functionalized by 11-mercaptoundecanoic acid and glass parts were functionalized with a PEG-silane. This double functionalization leads to a reactive gold surface, enabled to react with beads and to a passivated glass surface, unable to adsorb or react with beads.

The methodology for assembling, locating and grafting permanent microfilaments that we have developed and described in reference [1] was also successfully adapted to nanometric-scale. Fig. 2 shows permanent magnetic filaments obtained by assembling 200 nm diameter particles. These filaments were grafted covalently on the gold part of a mixed support thanks to the selective functionalization and could also be actuated.

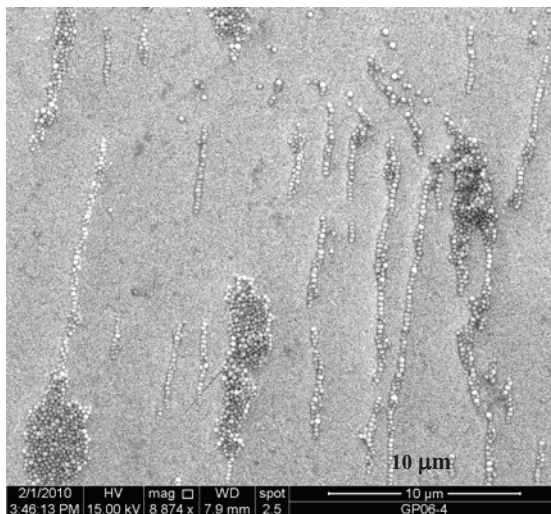


Fig 2: Permanent filaments covalently grafted on a gold surface and obtained by assembling 200 nm diameter particles. (SEM picture)

2.2. Anisotropy characterization by P-SPRI system

The micronic magnetic filaments assembled, located and grafted on gold support were then analysed with a new polarimetric surface plasmon resonance imaging (P-SPRI) system [2]. Actuation of micronic magnetic filaments was used as a mean to validate a biosensor capable to dynamically characterize anisotropy resulting from mean orientation of surface-bound assemblies (Fig. 3).

The anisotropy is characterized by a reflectivity difference (ΔR) between the two orthogonal arms of the sensor. When the magnetic filaments are oriented parallel to the surface, the reflective index at the surface changed. Due to their shape, filaments are anisotropic and therefore a change in the reflectivity difference should be observed when filament orientation also changed.

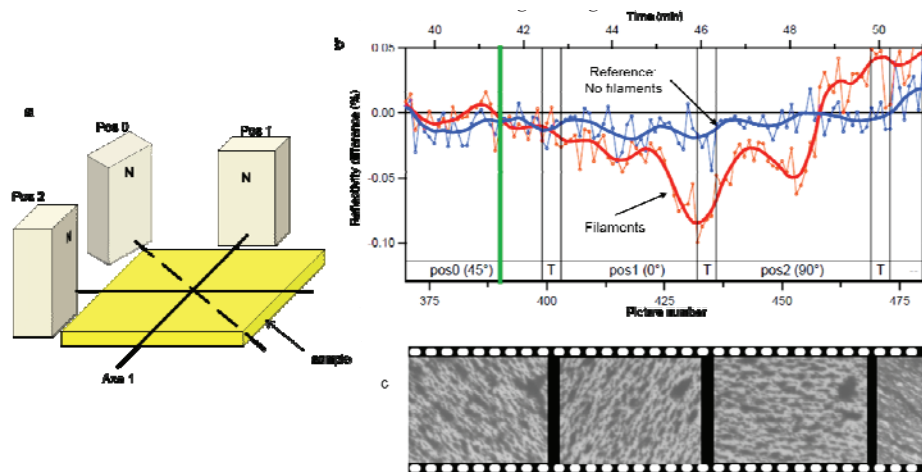


Fig. 3: (a) Magnet position used for filament actuation during the experiments for the validation of P-SPRI sensor. Pos0, Pos1 and Pos2 correspond respectively to 45°, 0° and 90° angle compared to axe 1. (b) Measurement of reflectivity difference with a polarimetric Surface plasmon Resonance Imaging sensor during the actuation of micronic permanent filaments. (c) Real-time actuation control by optical microscopy.

ΔR was compared for a reference spot (a spot without filaments) and a spot with filaments. Abrupt signal variations were observed when the magnet position and so the filament angle compared to axe 1 was changed. ΔR changed from a value of - 0.01% at 45° to a value of - 0.08% at 0°. This phenomenon was observed between 0° and 90°: from $\Delta R = - 0.08\%$ to $\Delta R = - 0.04\%$. First measurements tend to show that the filament anisotropy can be detected by the P-SPRI biosensor.

3. Conclusion

We developed a method to assembled permanently magnetic particles in filaments than can be grafted and localized by different methods on various supports. These filaments anchored to the surface by one extremity can also be actuated in a 2π solid angle. This property was used to validate a new P-SPRI system that is able to dynamically characterize anisotropy. Anisotropy is characterized by a reflectivity difference (ΔR) between the two orthogonal arms of P-SPRI sensor. Shifts of (ΔR) were measured as function of the orientation of filaments. That tends to show that anisotropy can be detected by the sensor.

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