



Nanowire manipulation on surfaces through electrostatic self-assembly and magnetic interactions

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A method for fabricating aligned nanowire arrays on surfaces is shown. Gold and segmented Au/Ni/Au nanowires of high aspect ratio have been prepared by template electrosynthesis, and functionalized with charged short alkanethiols that can be ionized in aqueous solutions. Different distributions of functionalized nanowires could be obtained on large surfaces from nanowire aqueous suspensions, avoiding aggregation due to

electrical repulsion. Due to the high magnetic anisotropy of segmented Au/Ni/Au nanowires chaining of aligned nanowires could be obtained by applying a low magnetic field. While electrostatics favours side wire interactions due to the high aspect ratio, concurrent electrostatics and applied magnetic field yields end-to-end interaction and linear alignment without bifunctionalization.

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Assembling building blocks in the nanoscale is the key to the design of novel systems with performance determined by objects of low dimensionality. In particular, fabrication, manipulation and positioning of asymmetric nanoobjects is a present challenge of nanochemistry [1]. In particular, a wide variety of one-dimensional nanostructures that display interesting and useful unique properties has been fabricated [2]. Interesting applications include chemical and biological sensors, nanoelectronic circuits, optical switches, logic circuits, etc.

Fabrication of nanostructures using different methods is a growing field of interdisciplinary research and the advances in fabricating nanoscale devices will depend on the ability to synthesize, deposit, and position *nano*-building blocks on suitably designed substrates. Among the fabrication techniques at hand, the electrochemical template synthesis of nanowires pioneered by Martin [3] has the ability to introduce specific individual segments along the length of the nanowire, resulting particularly attractive in designing objects with complex functions [4, 5]. One of these is the barcoded nanorod with segments that are able to bind specific biomolecules [6]. Using molecular linkages that bind specifically to different materials en-

ables spatially localized surface functionalization to be achieved [7–9].

Nanowires can be grown, suspended in solvent and then transferred onto substrates in a manner that bypassed the need for in situ growth. However, there is a trend to aggregate on surfaces due to the large surface area of high aspect ratio nanowires. This aggregation represents a very serious drawback to assemble individual nanowires under control. Therefore, it is important to reduce nanowire aggregation for technological application where a large number of them should be positioned on surfaces. External electric fields have been used to control the position and distribution of semiconductor [10] and metallic nanowires [11, 12]. The alignment and ordering of nickel or nickel-end nanowires has been controlled using external magnetic fields [13, 14] obtaining in addition nanowires aligned between contacts. Positioning directed by magnetic interaction of segmented Ni/Au/Ni nanowires with ferromagnetic ends and ferromagnetic contacts on a surface and magnetic alignment with an external field have been also reported [15]. On the other hand, selective assembly of thiol derivatized nanowires on functionalized surfaces has been achieved [16, 17] and a variety of alignment techniques,

have been reported [18]. It is worth mentioning the strategy of Searson and co-workers [19] who reported end-to-end directed positioning of aligned multisegment Au/Pt/Au and Au/Ni/Au nanowires using biotin–avidin linkage. However this strategy needed bifunctionalization to prevent lateral assembly and very short Au ends to allow for end-to-end chaining.

In the present paper we report the assembly, manipulation and positioning of segmented Au/Ni/Au nanowires by a combination of electrostatic self-assembly and magnetic interactions to produce chained nanowires in a single operation without the need to use bifunctionalization and with no limitation on the Au segment length. Furthermore, use of nanowires derivatized by short alkanethiols that can be ionized in aqueous solution avoids aggregation by electrostatic repulsion, while the combination of positively and negatively charged thiol Au/Ni/Au nanowires leads to lateral aggregation in the absence of an external magnetic field.

In a typical synthesis, we have employed an electrochemical template method to prepare nanowires (see Supporting Information, online at: www.pss-rapid.com). The typical dimensions of the resulting Au and Au/Ni/Au nanowires were about 180 nm diameter and about 6 μm in length with a large aspect ratio (length to diameter of 33). The template-free nanowires were finally suspended in Milli-Q water.

A fraction of the nanowires was further derivatised with 3-mercaptopropyl sulfonate (MPS) to obtain negatively charged nanowires while another fraction was derivatised with 2-mercaptoethylamine hydrochloride (MEA), to obtain positively charged nanowires. In these experiments the thiol is in large excess with respect to the concentration required for surface saturation. The derivatised nanowires were collected by repeated centrifuging and rising steps in order to remove excess of thiol. Finally the derivatised nanowires were redispersed in Milli-Q water reaching in all the samples the same nanowire concentration (see Supporting Information).

Deposition of Au and Au/Ni/Au nanowires on glass surfaces was carried out by drop cast from the aqueous nanowire suspension on a glass and dried at 50 °C. The Au/Ni/Au nanowires were also cast on glass but under the influence of a ca. 100 G magnetic field. After deposition the surfaces were rinsed with distilled water and dried in dry N_2 flow.

Derivatised gold nanowires show under the microscope a uniform distribution over large areas. The optical micrographs in Fig. 1 show the assembly of the gold nanowires on glass surfaces. As it is well known, non-derivatised nanowires dispersed in water were found to form spontaneously significant aggregation in a further assembly on the surface as it is depicted in a control experiment in Fig. 1a; some aggregation is probably from solution. However, derivatised nanowires with MEA and MPS show effective separation by mutual repulsion as observed in Fig. 1b and c, respectively, with a rather homogeneous distribution on a non-functionalized surface. It is believed that

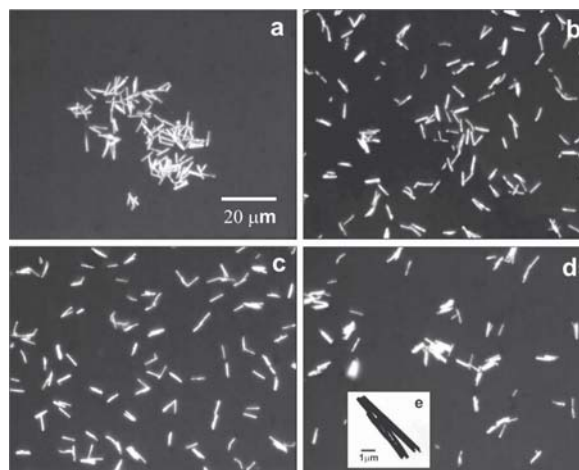


Figure 1 Optical microscopy by reflexion of gold nanowires assembled on glass substrate under different conditions: (a) as prepared Au nanowires; (b) Au-MPS derivatised nanowires; (c) Au-MEA derivatised nanowires; (d) mixture of Au-MEA and Au-MPS derivatised nanowires. Inset (e): Representative TEM image of arrays formed in Fig. 1d.

the distribution of Au nanowires is achieved via electrostatic interaction between the charge functional groups on the nanowires and fast solvent evaporating rate, minimizing the opportunity for nanowire aggregation to occur during evaporation, since for lower evaporation temperatures greater aggregation was observed.

Bundles of nanowires on the glass substrate were formed due to lateral interaction by dropping a 1:1 MPS/MEA derivatised nanowire ratio suspension as shown in Fig. 1d. Figure 1e depicts a representative TEM image of lateral interaction for the Au nanowires. This can be explained considering the electrostatic attraction between the negatively charged sulfonate (SO_3^-) group in the MPS modified nanowires and the positively charged ammonium (NH_4^+) group in the MEA modified nanowires due to the high length to diameter ratio.

Due to their shape and size the Au/Ni/Au nanowires have a large magnetic anisotropy and this can favour the assembly under the influence of a magnetic field. Pure nickel nanorods have been assembled in this way into chains using a magnetic field parallel to the substrate in a high viscosity liquid such as 1:1 hexadecane/octane mixtures or ethylene glycol [14]. In our hands, the incorporation of a central Ni segment in the multisegment Au/Ni/Au nanowires has been important to control the end-to-end position under an external magnetic field of the otherwise electrostatically laterally interacting nanowires. Non-chemically modified segmented Au/Ni/Au nanowires can be oriented parallel to the field in an external magnetic field as shown by optical reflexion in Fig. 2a on a glass surface with substantial lateral aggregation of the unmodified nanowires. A slightly lower alignment was observed in MPS or MEA derivatised nanowires. However, the concurrent effect of electrostatic attractions between nano-

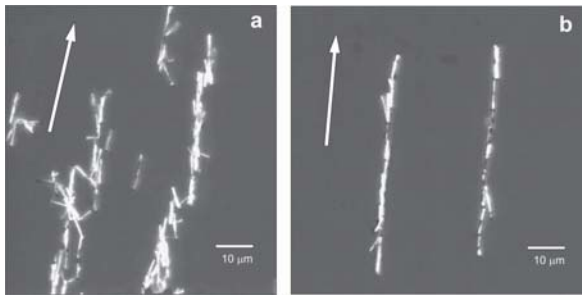


Figure 2 Optical microscopy by reflexion of Au/Ni/Au nanowires on glass surface oriented under magnetic field: (a) with no derivatising, (b) mixture of MEA and MPS derivatised nanowires. The arrow indicates the magnetic field orientation.

wires with different functionalization and the orientation of the central nickel segments in the external magnetic field, yields a remarkable enhancement of the nanowire alignment as shown in Fig. 2b for a 1 : 1 ratio of a suspension of a mixture of Au/Ni/Au nanowires chemically modified respectively by MEA and MPS and drop cast on a glass surface. The experiments conducted are summarized in Table 1.

The improvement for derivatised nanowires, narrow chains that can be extended over tens of micrometers on the base glass surface may be attributed to the oppositely charged Au segment by selective thiol functionalization [7] that would prevent the angular dependence of the dipolar forces between randomly oriented nanowires. It is worth mentioning that these behaviours are also obtained on silicon wafers.

These results represent the first disclosure to our knowledge of the combination of magnetic forces and surface thiol derivatization to manipulate and position nanowires on surfaces. It is important to emphasize the use of water as the solvent in this technique for the assembling of nanowires that makes it compatible with biological systems such as cell and enzymes without affecting their bioactivity.

In summary, we have introduced a method that allows spatial manipulation and positioning of segmented metal nanowires on non-functionalized surfaces by combination of electrostatic interactions of functional alkanethiol chemically modified Au segments in multisegment nanowires with the orientation of the ferromagnetic segments in an external low magnetic field and solvent dewetting. In this method we are not limited to short-end Au segments to bind end-to-end the nanowires since this is achieved by the orientation of the ferromagnetic central segments. We also avoided the use of bifunctionalization by selectively binding molecules to

Table 1 Alignment data for Au/Ni/Au and Au/Ni/Au derivatised nanowires oriented under magnetic field.

Au/Ni/Au nanowires	nanowires aligned
with no derivatising	63% (226 of 360)
MPS derivatised	51% (168 of 330)
MEA derivatised	54% (189 of 350)
mixture of MEA and MPS	92% (340 of 370)

different metals to prevent lateral assembly. Furthermore, the side thiolated functionalities can be used to tether biomolecules such as enzymes in aqueous environments. The method is simple and cost effective for high density interconnects, biosensors, logic circuits and other devices.

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