

Shaping Template-Assisted Organic Nanowires

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Nanowires have attracted a considerable attention in nanoscience. Among the nanowire fabrication techniques, the template-based method is one of the most attractive as it has proven to be reliable for the synthesis of nanomaterials having desired composition, size and aspect ratio. However, for many technical applications it is necessary to grow nanowires at defined positions.

We report on a novel approach for patterning vertical semiconducting polyaniline (PANI) nanowires with an unprecedented areal patterning density exceeding 0.25 teradot/inch². A simple few-steps process is put forward to hierarchically build a large variety of functional polyaniline nanowire arrays on virtually any type of flexible or rigid substrates. Using template confinement, through Pt catalyzed electroless growth, highly-organized arrays of distinct polyaniline nanowires are produced with a typical diameter of 15 nm and aspect ratio higher than 20. Complex three-dimensional structural control is achieved through a direct pattern transfer using a novel type of resist- and dose-modulated electron beam lithography [1].

The morphology-modulated polymer nanowires are driven to self-assemble in key-lock type architectures orchestrated by the structural asymmetry and non-uniformity of the capillary forces. This asymmetry provides the potential of being further exploited for spherical, helical or tubular functional macroassemblies. Combined with the modulated optoelectronic properties and the straightforward mechanical actuation of the polyaniline, these assemblies could play a role in the design of stimuli-responsive smart materials for biosensing.

Aspects of the PANI growth mechanism at nano-scale are discussed and the remarkably controllable, sub-picogram scale fabrication is emphasized. We designed a novel type of nanoscale electro-polymerization reactors. The concept is close to nanochemistry methods allowing chemical reactions to be carried out on ultra-small amounts of mater, that are of increasing interest due to their potential in solving many industrial (such as energy consumption and waste management) as well as fundamental science (molecular electronics, biochemistry and physico-chemistry in confined media) challenges. The nano-electrochemistry modus operandi is unique as it allows reliable patterning, growth and processing of polyaniline nanowires with ultimate resolution. Via a combinatorial nanochemistry approach [2], we highlighted the salient features of the single PANI nanowire manufacturing and of the device-integrated polymerization process.

Finally, we used the electronic nanolithography for the precise positioning of single nanowires in microsystem-integrated PMMA matrices. The as-synthesized polyaniline nanowires display electric conductivities reaching values as high as 0.4 S/cm.

Notably, we studied the electrical behavior of single vertical polyaniline nanowires embedded in PMMA matrices and addressed the fabrication of crossbar latches using a criss-cross arrangement of electrodes. This opened the way for the realization of all-organic, high-density (teradot/inch²) molecular memories [3].

We discuss next planar nanowires of oriented discotic phthalocyanine molecules. Local orientational control of discotic molecules forming columnar mesophases is a key issue in the preparation of organic devices. We have developed a novel method for orienting planar nanowires of discotic phthalocyanines. The method relies on the fabrication of a network of perpendicular nanotrenches of increasing spacing and constant width. This network is then filled with phthalocyanines and flash-annealed. For wide-enough trenches it is possible to obtain a constant and regular thickness of nanowires all over the network. The orientation of the columnar mesophase is then governed by the balance of surface energies at orientational freezing, and can be modelled with simple equations. For small trench widths, however, a partial coupling of the width of perpendicular trenches occurs. Under these circumstances, the repartition in the trenches of the phthalocyanines in the isotropic phase is governed by capillary action, with various capillary rises in different parts of the network. This results in an inhomogeneous thickness of nanowires over the network. In this so-called non-constant thickness regime, discotic columns are also uniformly oriented, but are now perpendicular to the direction that would be obtained in the constant thickness regime. The inversion of orientation can be explained by the same equilibrium equations as in the constant thickness regime, and a global model capable to describe the whole set of observations is proposed [4,5].

Finally, planar nanowire networks of discotic phthalocyanines were inserted into field-effect transistors as conduction channels. We measured samples with columns parallel and perpendicular to source-drain electrodes and observed an anisotropy of currents consistent with the literature. We showed that the weakness of the measured signal can be partially explained by a reduction in the effective cross-section of the nanowires contributing to the charge transport. This reduction arises for any field-effect transistor made of nearly parallel nanowires running from source to drain.

References:

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